PORTLAND CEMENT

Its Composition, Raw Materials, Manufacture, Testing and Analysis

BY

FRANKLIN INSTITUTE
PHILADELPHIA

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PREFACE TO FIRST EDITION.

The present treatise upon Portland cement is really the second edition of a small manual by the writer, published some four years ago, called "The Chemical and Physical Examination of Portland Cement." In preparing this new edition, it seemed wise to add a section on the manufacture of Porland cement, for the reason that the chemist who is to intelligently supervise the process of manufacture, as well as the chemist who is to report upon the raw materials and the engineer who is to inspect the product, should have a good, general knowledge of the technology of Portland cement.

It was also found necessary to rewrite almost the entire section upon the physical testing of cement in order to give special prominence to the uniform methods of testing adopted by the American Society of Civil Engineers, and to the standard specifications of the American Society for Testing Materials. Much new matter has also been added to the section on the analysis of cement and its raw materials, and sections on the experimental manufacture of small lots of cement and on the history of the industry have been included.

The analytical methods have all been used to some extent in the writer's laboratory and have been found satisfactory. Comments as to their accuracy and advice as to the best methods of manipulation will usually be found with each method under the heading, "notes."

The author again wishes to thank the many friends who have aided him in the preparation of both this and the former edition.

NAZARETH, PA., July, 1906.

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PREFACE TO THE SECOND EDITION

In the preparation of the present edition, the entire text of the book has been revised. Much new matter has been added, particularly to the section on "Manufacture," which has been increased by 76 pages. Descriptions of the newer appliances for the Manufacture of Portland Cement have been added so that it is believed that this section represents fairly well the present state of the industry in this country.

The section on "Analytical Methods" has been somewhat condensed, so far as space goes, by the printing of the notes in smaller type but the actual matter has been increased. The section on "Physical Testing" has been revised to conform to the changes made in the standard specifications and methods of testing, and much new matter has been included here also.

A chapter has been added to the book on the "Investigation of Materials for the Manufacture of Portland Cement." The number of illustrations has been increased from 100 to 170 and among the new ones will be found many half-tones showing actual installations of cement machinery, kilns, etc.

BALTIMORE, MD., October, 1911.

PREFACE TO THE THIRD EDITION

Originally this work was intended primarily for chemists and cement inspectors and described methods of test and analysis only. The section on the manufacture of cement has been increased with each edition, however, until now it is much the largest part of the book. It is hence believed that the work will prove fully as useful to engineers and others interested solely in the mechanical features of the process as to chemists and others engaged in inspecting and testing cement.

In preparing the third edition of this book, the author has taken the opportunity to again thoroughly revise the entire text to make it conform to present day theory and practice. Much of the book has been rewritten. The subject matter has been increased by nearly two hundred pages, most of this new material being added to the section on "Manufacture." Seventy new illustrations appear in this and it is believed that it covers all of the latest advances in the art of cement making, including the waste heat boiler, dust precipitation, etc. An effort has been made to present the manufacture of cement in as practical a manner as possible and much information is given as to the power and fuel requirements of the process, output of machines, cost data, etc.

A few new methods of analysis have been added to the section on "Analytical Methods" and the section on "Physical Testing" has, of course, been revised to agree with the present American standard specifications and methods of test. Paragraphs have been added at the end of each chapter of this showing the influence of manufacturing conditions, chemical composition, etc., upon those properties of cement covered by the tests. This has been done with a view to presenting in brief form methods for correcting faults in manufacture. Some information as to foreign specifications, methods of test, etc., has also been added to this section.

Once more, the author wishes to express to his many friends in the cement industry his appreciation and thanks for the assistance they have given him in the revision of this book. Their kindness in furnishing him with the results of their experience has done much to add to its value.

BALTIMORE, MARYLAND, June, 1926.

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INTRODUCTION

CHAPTER I

RELATION BETWEEN MORTAR MATERIALS AND HISTORY OF THE DEVELOPMENT OF THE AMERICAN PORTLAND CEMENT INDUSTRY

Relation Between Portland Cement and Other Mortar Materials

Mortar materials may be classified according to their properties, methods of manufacture and materials from which they are made as follows:—

1. *Common Limes* are made by burning relatively pure limestone. When mixed with water they slake and show no hydraulic properties.

2. *Hydraulic Limes* are made by burning impure limestone at low temperatures. They slake with water but show hydraulic properties.

3. *Natural Cements* are made by burning impure limestones at a low temperature (insufficient to vitrify). They do not slake with water but require to be ground in order to convert them into a hydraulic cement.

4. *Portland Cement* is made by heating to incipient vitrifaction an intimate mixture of an argillaceous substance, such as clay or shale, and a calcareous substance, such as limestone or marl, in which mixture the percentage of silica, alumina and iron oxide bears to the percentage of lime the ratio of approximately 1 : 2, which vitrified product does not slake with water but upon grinding forms an energetic hydraulic cement.

5. *Puzzolan Cements* are made by incorporating slaked lime with finely ground slag or volcanic ash or by incorporating a small proportion of Portland cement clinker with suitably treated slag and grinding intimately the mixture.

6. *Plasters* are made by heating gypsum sufficiently to drive off three-fourths or all of the combined water which it contains and grinding finely the more or less dehydrated residue.

Table I given below will explain the above classifications, while Tables II and VIII show the composition of these various materials.

TABLE I.—SHOWING THE RELATION BETWEEN LIMES, CEMENTS AND PLASTERS.

Raw materials	Chemical treatment	Mechanical treatment	Hydraulic properties	Classification
Made from relatively pure limestones	Burned at low temperatures. 600°-1200° C.	Slake on addition of water to burned product	Not hydraulic	1. Common lime
Made from argillaceous or impure limestone			Hydraulic	2. Hydraulic limes
		Do not slake on addition of water but must be ground finely for use		3. Natural, Roman or Rosendale cement
Made from an intimate mixture of argillaceous and calcareous substances in proper proportions	Burned at high temperatures. 1300°-6100° C.			4. Portland cement
Made from mixtures of slaked lime and blast furnace slag or volcanic ash	Not burned			5. Slag or Puzzolan cements
Made from gypsum	Burned at from 165-200° C.		Not hydraulic	6. Plasters

TABLE II.—Chemical Composition of Mortar Materials.

Material	From	Analysis							
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	CO_2	H_2O
Lime	Glencoe, Mo	0.15	0.85		98.01	0.45	..	0.55	..
Lime	York, Pa.	0.52	0.24		97.14	1.28	..	0.96	..
Lime	McNeil, Tex	0.25	0.15		97.46	0.73	..	1.41	..
Lime	Tiffin, O.	1.61	0.17		57.44	40.36	..	0.41	..
Hydrated lime	Carey, O.	0.34	0.18		45.37	31.20	..	3.02	20.07
Hydrated lime	Union Bridge, Md.	0.38	0.08	0.06	72.59	0.74	..	2.10	23.11
Hydraulic lime	Lafarge Cement	31.10	2.15	4.43	58.38	1.09	0.60	1.28	..
Hydraulic lime	Teil, France	19 05	0.55	1.60	65.10	0.65	0.30	..	12.45
Plaster of Paris	Nova Scotia.	0.11	0.01	0.03	38.90	0.14	54.81	0.54	5.33
Plaster of Paris	Buffalo, N. Y.	2.48	0.32	0.40	37.81	0.39	53.12	0.61	4.98
Natural cement	Cumberland, Md.	29.92	4.78	11.23	36.50	11.93	..	5.42	..
Natural cement	Rosendale, N. Y.	27.75	4.28	5.50	35.61	21.18	0.50	4.05	..
Portland cement	Average American	22.56	2.85	7.44	62.73	1.99	1.46	..	..
Portland cement	Average German	21.29	2.72	7.64	63.48	1.53	1.77	..	..
Portland cement	English, "K. B. & S."	19.75	5.01	7.48	61.39	1.28	0.96	..	..
Portland cement	Belgian, "Josson"	22.92	2.46	7.98	63.39	trace	1.28	..	..

History of the Development of Mortar Materials

When lime mortar was first employed or what people discovered its binding properties no one knows, but it is certain that its use antedates written history. It has been found between the stones of what remains of a very ancient temple on the Island of Cyprus, supposed to be the oldest ruin in the world. The Egyptians used, in place of lime, a mortar in which partially burned gypsum or plaster of Paris was the cementing factor and this was employed in the construction of the Pyramids, built over four thousand years ago. The Romans discovered that a mixture of lime and volcanic ashes would harden under water and hence might be used for the construction of aqueducts, cisterns, docks, etc. They used this mortar in many of their public buildings and temples, in the Phantheon, in the Baths of Caracalla and in the aqueduct which supplied Rome with water. From the period of the Romans, no advance was made in the technology of building materials until the latter part of the eighteenth century, when the modern cement industry had its beginning .

The Beginning of the Cement Industry in England

The cement industry proper dates from the researches of an English engineer, John Smeaton, who had been employed by parliament to build a lighthouse upon a group of gneiss rocks, in the English Channel, just off the coast of Cornwall. These crags, known as Eddystone, were at high tide under water for some hours and many shipwrecks had occurred upon them. They were a menace to the navigation of this part of the channel and it was necessary to warn sailors of their whereabouts. Two wooden structures built upon them had been subjected to the fury of the elements and had each experienced a short life.

When Smeaton attacked the problem, he determined to build a structure which would weather the fiercest storms of the channel and would come out of these an enduring monument to his engineering skill. One of the greatest difficulties he had to overcome was the failure of ordinary lime mortar (the discovery of which dates back to antiquity) to harden under water. In order

that his foundations should be firm, it was necessary that some mortar be found which would meet this difficulty. To this end he undertook a series of investigations in 1756, the result of which was the discovery that the hard, white, pure limestones, hitherto considered best for lime making, were in reality inferior to the soft clayey ones;[1] for from these latter he succeeded in obtaining a lime far superior to any then in use because it not only hardened better in air, but would also harden under water. Such a limestone Smeaton found near at hand, at Aberthaw, in Cornwall, and the hydraulic lime formed by burning this stone was the basis of the mortar used in the construction of the Eddystone lighthouse.

Smeaton in making his hydraulic lime, however, used only those layers of his quarry which after burning gave a product that would slake with water. The idea of burning the layers which would not slake readily and then by grinding, convert them into a very energetic hydraulic lime did not suggest itself to him and it was not until forty years later that this first improvement was made in the manufacture of hydraulic lime.

In 1796, one Joseph Parker, of Northfleet, in Kent Co., Eng., took out a patent for the manufacture of a hydraulic lime which he called "Roman Cement" and which he made by calcining or burning the argillocalcareous, kidney-shaped nodules called "septaria" and then grinding the resulting product to a powder.[2] In composition these nodules were very similar to what we now call Rosendale cement-rock. They occurred geologically in the London clay formation and were usually obtained from the shores of the Isle of Sheppy where they were washed up after a storm. This cement came rapidly into favor with the English engineers because much work could be done with it that was impossible with quicklime. In 1802 cement was produced from the same "septaria" at Boulogne, France, and this was the beginning of the cement industry in that country.

In 1810, Edgar Dobbs, of Southwick, England, obtained a patent for the manufacture of an artificial Roman cement by

[1] Smeaton—Narrative of the building, etc., of the Eddystone Lighthouse, Book IV.
[2] Redgrave—Calcareous Cements.

mixing carbonate of lime and clay, in suitable proportions, moistening, molding into bricks, and burning sufficiently to expel the carbonic acid, without vitrifying the mixture. Soon after this, General Sir Wm. Paisley, in England, and L. J. Vicat, a French engineer, both independently of each other, made exhaustive experiments looking to the manufacture of an artificial Roman cement by mixing clay with chalk, etc. In 1813 Vicat began the manufacture of artificial hydraulic cement in France, as did also James Frost in England, in 1822.

Invention of Portland Cement

In 1824, Joseph Aspdin, a bricklayer of Leeds, England, took out a patent on an improved cement which he proposed to make from the dust of roads repaired with limestone, or else from limestone itself combined with clay, by burning and grinding. This cement he called "Portland Cement," because when hardened it produced a yellowish gray mass resembling in appearance the stone from the famous quarries of Portland, England.

Aspdin is usually credited with the invention of Portland cement and while he certainly did originate the name "Portland Cement" he probably did nothing more than make an artificial Roman cement, which had been done before, since he apparently did not carry his burning to the point of incipient vitrifaction, which we now recognize as being an essential point in the manufacture of Portland cement.[1] Aspdin erected a factory at Wakefield, England, for the manufacture of his cement, which was used upon the Thames Tunnel in 1828. At first Portland cement was sold at prices considerably lower than the Natural or Roman Cement of Parker and his successors, and it was not until John Grant, in 1859, decided to use Portland cement in the construction of the London drainage canal, of which he was chief engineer, and published his reasons for doing so in the transactions of the Institute of Civil Engineers, that the new cement began to come to the front.

It is evident that by this time the value of burning the clinker to the point of incipient vitrifaction had been discovered and

[1] Michaelis—*Thonindustrie Zeitung*, Jan. 16, 1904.

made use of—probably first in the famous old works of White & Bros., established by James Frost at Swanscombe, in 1825, and still existent. In 1852 the first German Portland cement works were established near Stettin. The Germans were quick to see the value of the new building material, and with their fine technologists soon turned out a better product, by the substitution of scientific methods in place of rules of thumb. They were the first to appreciate the value of fine grinding of the cement, and until recently the German Portlands were the standards. To-day undoubtedly the best Portland cement made in the world is turned out in America.

Discovery of Cement-Rock in the United States

In this country the cement industry began with the discovery in 1818, of a natural cement-rock near Chittenango, Madison Co., N. Y., by Mr. Canvass White, an engineer engaged in the construction of the Erie canal, who after some experimenting applied to the State of New York for the exclusive right to manufacture this cement for twenty years. The state denied his request but gave him $20,000 in recognition of his valuable discovery.[1] His cement was used in large quantities in the construction of the Erie canal and brought a price of about twenty cents a bushel.

As the greatest users of cement in this country were the canals, and as they at that time furnished the only means for the transportation of bulky materials, there was naturally the sharpest lookout kept along their line of construction for limestone suitable for the making of hydraulic cement. In consequence of this, nearly all the early cement mills were started along the line of, and to furnish cement for, the construction of some canal. In 1825, cement-rock was discovered in Ulster County, New York, along the line of the Delaware and Hudson canal and in the following year a mill was started at High Falls in that county. In 1828, a mill was built at Rosendale, also in Ulster County. This soon became the center of the industry and the cement made here was called Rosendale. This name is still largely applied to American natural cements. The first cement was made in small upright

[1] Sylvester—History of Ulster County, N. Y.

kilns. Wood was used as fuel and the burning continued for about a week. The clinker was then ground between mill stones by water-power. After these mills had been in operation several years continuous kilns were introduced which permitted the clinker to be drawn daily, coal being used as fuel.

In 1829 cement-rock was discovered near Louisville, Ky., while constructing the Louisville & Portland Canal, and John Hulme & Co. almost immediately began the manufacture of Louisville cement at Shippingport, a suburb of Louisville.[1]

During the construction of the Chesapeake and Ohio Canal, cement-rock was discovered, in 1836, in Maryland, at Round Top, near Hancock, and it has been manufactured there ever since. Other canals along whose lines cement-rock was discovered with the location and date, are the Illinois and Michigan Canal, at Utica, in 1838; James River Canal, at Balcony Falls, Va., in 1848; and Lehigh Coal and Navigation Co. Canal, at Siegfried, Pa., in 1850. At all of these points the manufacture of cement has been continuous. Other well known brands of cement began to be manufactured as follows: Akron, N. Y., 1840; Ft. Scott, Kan., 1868; Buffalo, N. Y., 1874; and Milwaukee, Wis., in 1875.

Manufacture of Natural Cement

The process for making natural cement is in general as follows: The rock is blasted down from the face of the quarry, broken by hand with sledges into sizes suitable for the kiln, loaded on dump cars and elevated to the mouth of the kilns. Here the rock is dumped into the kiln alternately with coal, a layer of rock and then a layer of coal. The charging is kept up continuously during the daytime but hardly ever at night. As the charge works its way down through the kiln it becomes calcined and the larger portion of its carbonic acid driven off. When it reaches the base of the kiln it is drawn out and conveyed to the grinding machinery. The kilns used for the manufacture of natural cement are usually made of iron plates riveted together and lined with firebrick. They are circular in shape, upright, and their average dimensions are about 16 feet in diameter by 45 feet in height.

[1] Lesley—*Jour. Assoc. Eng. Socs.*, **15**, 198.

The clinker is usually ground by buhr-stones, the fine material in many mills being separated from the coarse by passing over screens, so placed as to allow the fine particles to go to the storehouse and to return the coarse ones to the grinders. The buhr-stones are preceded by crushers or crackers to reduce the clinker to a suitable size for them to handle. In some instances ball and tube mills and Griffin mills have been installed in natural cement plants, particularly where these plants also make Portland, but the clinker from these kilns is usually so soft as to be easily ground by buhr-stones.

There were at one time in this country between 60 and 70 mills manufacturing natural cement, now there are very few in operation. The principal use of natural cement to-day is for laying brick and stone. The terms "masonry cement" and "brick cement" and various trade names are now often applied to natural cement alone or to mixtures of natural cement with hydrated lime and other substances added to give plasticity.

Below are some figures on the production of natural cement in this country.

TABLE III.—Production of Natural Cement in United States, 1818–1915.

(Mineral Resources of the United States, 1915.)

Year	Barrels	Year	Barrels	Year	Barrels
1818 to 1830	300,000	1888	6,253,295	1902	8,044,305
1830 to 1840	1,000,000	1889	6,531,876	1903	7,030.271
1840 to 1850	4,250,000	1890	7,082,204	1904	4,866,331
1850 to 1860	11,000,000	1891	7,451,535	1905	4,473,049
1860 to 1870	16,420,000	1892	8,211,181	1906	4,055,797
1870 to 1880	22,000,000	1893	7.411,815	1907	2,887,700
1880	2,030,000	1894	7,563,488	1908	1,686,862
1881	2,440,000	1895	7,741,077	1909	1,537,638
1882	3,165,000	1896	7,970,450	1910	1,139,239
1883	4,190,000	1897	8.311,688	1911	926,091
1884	4,000,000	1898	8,418,924	1912	821,231
1885	4,100,000	1899	9,868,179	1913	744,658
1886	4,186,152	1900	8,383,519	1914	751,285
1887	6,692,744	1901	7,084.823	1915	750,863

It will be noticed that there was but little increase in the production of natural cement from 1887 to 1903 and that since the

latter date there has been a steady decline. This is due to the fact that since about 1900 Portland cement has been fast displacing natural cement. The increase in production in 1900 was due to the strong demand for building materials that year; a demand that could not be supplied by the Portland cement manufacturers. Our imports in 1900 were over 3,000,000 barrels of Portland, in spite of the fact that the home mills produced over 3,000,000 barrels more than in 1899.

Beginning of the Portland Cement Industry in the United States

As we have stated cement-rock was discovered in 1850 at Siegfried, in Northampton Co., Pa., on the line of the Lehigh Coal and Navigation Co.'s canal leading from Easton to Mauch Chunk. As the cement for the canal had to be brought from New York, the discovery was a valuable one and was put to immediate use by the erection of a mill at Siegfried.

In the spring of 1866, Messrs. David O. Saylor, Esaias Rehrig and Adam Woolever, three gentlemen, of Allentown, Pa., formed the Coplay Cement Co., and located a mill at Coplay, near Allentown, and not far from Siegfried. Mr. Saylor was president and superintendent of the company. The plant made excellent cement though its methods for doing so were crude. Early in the seventies Mr. Saylor began to experiment upon the manufacture of Portland cement from the rocks of his quarry. No Portland cement was made in this country then, and most of it in use here came from England and Germany. Its reputation was established and it was looked upon as superior to Rosendale cement.

Mr. Saylor was led to make his experiments by the fact that he noticed the harder burned portions of his Rosendale clinker gave a cement which for a short period would show a tensile strength equal to that of the best imported Portland; but he found this cement would crumble away with time. This was due to the raw materials not being properly proportioned. The result of these experiments taught him that if he mixed a certain amount of cement-rock high in lime with his ordinary cement-rock he could make Portland cement, and after many trial lots were burned the

company turned out its first Portland in 1875. This was the first Portland cement made in the Lehigh District, and it was made from a material totally different from that used in any of the European mills.

The drawings for the first kilns were made by James Cabott Arch, an English engineer, and were bottle-shaped.

Having solved the problem of how to make Portland cement, Saylor found another and equally difficult one awaiting him of how to sell it, after it was made. The labor cost of manufacturing his cement was great and he could not afford to offer it at prices much below the imported article. As the foreign cements had an established record, they fought the new cement with the argument that any brand of Portland cement required time to prove itself, and it was only by liberal advertising and an iron-clad guarantee of his product that Saylor secured a market.

Among the first great engineering works upon whose construction Saylor's Portland cement was used were the Eads jetties along the Mississippi River, and the first great sky-scraper in which American Portland cement was used was the Drexel Building in Philadelphia. Slowly American Portland cement overcame the prejudice against it and it is now recognized as superior to that manufactured in any part of the world. Saylor's original plant turned out only 1,700 barrels of Portland cement a year. Since its inception, however, it has grown steadily and now has a capacity of considerably over this amount a day.

Development in Other States

While Saylor was conducting his experiments in the Lehigh Valley, a Chicago concern, known as the Eagle Portland Cement Co., built a plant near Kalamazoo, Mich., about 1872, to manufacture Portland cement from marl and clay. This plant at first consisted of two bottle-shaped kilns, which number was afterwards increased to four. The product was known as "Eagle Portland Cement," and its quality must have been excellent as some three or four miles of sidewalk put down in Kalamazoo are still in good condition. This mill, however was forced to shut down in 1882, for although its product sold at from $4 to $4.25

per barrel, it could not manufacture cement at a figure below this. To-day no traces of even the kilns remain.[1]

At Wampum, Pa., a small plant was started to make cement from limestone and clay, in 1875. Thomas Millen found, at South Bend, Ind., a white marl and clay which resembled in composition, the material used for cement making in England, and started a small plant there in 1877.[2] Both the plants at Wampum and South Bend, Ind., were for many years producers, though in a modest way. In Maine also a small plant was started by the Cobb Lime Co., at Rockport, in 1879, but this too failed to make cement at a figure below its selling price and closed down permanently as did also a small plant in the Rosendale district about the same time.

Of the six works started prior to 1881 half that number were failures and represented a complete loss to their promoters. The cement made at Coplay and Wampum, however, was on exhibition at the Philadelphia Centennial in 1876 and held its own with the imported article.

About 1883, a small plant for the manufacture of Portland cement was inaugurated at Egypt, Pa., near Coplay, by Robt. W. Lesley, the first president of the, to be later formed, American Association of Portland Cement Manufacturers, John W. Eckert, Saylor's first chemist, and others. This plant progressed gradually and developed into the American Cement Co., a large producer of both natural and Portland cement. From this time on plants sprung up rapidly in the Lehigh Valley Section, among the older ones being the Atlas, Bonneville, Alpha and Lawrence, all except the second now important producers.

In other sections also, successful mills were built. In New York, Thomas Millen, who had previously built a works in Indiana, and his son, Duane Millen, started the Empire Portland Cement Co., at Warners, Onondaga Co., in 1886. In Ohio, at Harper, Logan Co., the Buckeye Portland Cement Co., put in operation their plant in 1889; and in 1890 the Western Portland Cement Co., of Yankton, S. D., began to make Portland cement.

[1] Russell—Twenty-second Annual Report, U. S. Geological Survey, Part III.

[2] *Cement Age*, July, 1905, contains an interesting account by Mr. Millen himself of how he came to go into the manufacture of Portland cement at South Bend.

From this time on the Portland cement industry has taken rapid strides and plants have been built in almost every part of the country. The process of manufacture has been greatly improved, resulting in a considerable lessening of the cost of production. American Portland cement has practically displaced the imported article. New uses have been found for Portland cement and it is to-day, next to steel, our most important material of construction. The Portland Cement Association formed in 1902, has done wonders for the industry. This association has published and distributed gratis to those interested valuable bulletins explaining certain particular forms of concrete construction and the employment of cement by the farmer and artesan.

The American Concrete Institute has also been a potent factor in popularizing the use of concrete. This society holds an annual meeting at which papers dealing with cement products and concrete are read. In addition to the national association there are a number of local and state associations. Cement shows have been held at intervals at Chicago and in New York at which various appliances of use to cement workers were on exhibition as well as novel cement products, etc. At the present time, 1923, the United States produces about one-half the estimated production of the world. This is estimated as follows:

	Barrels
United States	137,000,000
Germany and Austria	30,000,000
British Empire	35,000,000
France and Colonies	12,000,000
Japanese Empire	12,000,000
Belgium	10,000,000
Others	30,000,000
Total	266,000,000

Table IV shows the growth of the American Portland cement industry from year to year. Table V the production by districts and states in 1922. Table VI the price from 1870 to 1922, and Table VII the growth of the per capita consumption.

TABLE IV.—Production of Portland Cement in the United States, 1870-1923, in Barrels.

Year	Quantity	Value	Year	Quantity	Value
1870-1879	82,000	$ 246,000	1901	12,711,225	$ 12,532,360
1880	42,000	126,000	1902	17,230,644	20,864,078
1881	60,000	150,000	1903	22,342,973	27,713,319
1882	85,000	191,250	1904	26,505,881	23,355,119
1883	90,000	193,500	1905	35,246,812	33,245,867
1884	100,000	210,000	1906	46,463,424	52,466,186
1885	150,000	292,500	1907	48,785,390	53,992,551
1886	150,000	292,500	1908	51,072,912	43,547,679
1887	250,000	487,500	1909	64,991,431	52,858,354
1888	250,000	487,500	1910	76,549,951	68,205,800
1889	300,000	500,000	1911	78,528,637	66,248,817
1890	335,500	704,050	1912	82,438,096	67,016,928
1891	454,813	967,429	1913	92,097,131	92,557,617
1892	547,440	1,153,600	1914	88,230,170	81,789,368
1893	590,652	1,158,138	1915	85,914,907	73,886,820
1894	798,757	1,383,473	1916	91,521,198	100,947,881
1895	990,324	1,585,830	1917	92,814,202	125,670,430
1896	1,543,023	2,424,011	1918	71,081,663	113,730,661
1897	2,677,775	4,315,891	1919	80,777,935	138,130,269
1898	3,692,284	5,970,773	1920	100,023,245	202,046,955
1899	5,652,266	8,074,371	1921	98,842,049	180,778,415†
1900	8,482,020	9,280,525	1922	114,789,984	207,170,430†
			1923*	137,377,000	

* Estimated.

† Value of cement shipped.

TABLE V.—Portland Cement Produced in the United States, by Districts and States in 1922.

Mineral Resources of the United States.

Commercial District	Production	
	Active plants	Quantity (barrels)
Eastern Pennsylvania, New Jersey, and Maryland	22	31,195,617
New York	9	5,922,706
Ohio, western Pennsylvania, and West Virginia	10	10,753,301
Michigan	12	6,243,805
Illinois, Indiana, and Kentucky	10	17,998,914
Virginia, Tennessee, Alabama, and Georgia	8	5,954,043
Eastern Missouri, Iowa, and Minnesota	9	11,392,552
Western Missouri, Nebraska, Kansas, and Oklahoma	11	8,025,720
Texas	5	3,628,756
Colorado and Utah	5	2,020,784
California	9	8,711,515
Oregon, Washington, and Montana	9	2,942,271
	118	114,789,984

TABLE V.—PORTLAND CEMENT PRODUCED IN THE UNITED STATES, BY DISTRICTS AND STATES IN 1922. (*Continued*)

State	Production	
	Active plants	Quantity (barrels)
Alabama	3	2,290,884
California	9	8,711,515
Illinois	4	6,407,129
Iowa	4	4,272,432
Kansas	7	4,634,287
Michigan	12	6,243,805
Missouri	5	6,170,633
New York	9	5,922,706
Ohio	5	2,835,243
Pennsylvania	22	33,276,093
Texas	5	3,628,756
Washington	4	1,942,781
Other States (*b*)	29	28,453,720
	118	114,789,984

(*b*) Colorado, Georgia, Indiana, Kentucky, Maryland, Minnesota, Montana, Nebraska, New Jersey, Oklahoma, Oregon, Tennessee, Utah, Virginia, and West Virginia.

TABLE VI.—AVERAGE PRICE PER BARREL OF PORTLAND CEMENT, 1870-1922.

Year	Price	Year	Price	Year	Price
1870-1880	$3.00	1897	$1.61	1911	$0.844
1881	2.50	1898	1.62	1912	0.813
1882	2.01	1899	1.43	1913	1.005
1883	2.15	1900	1.09	1914	0.927
1884	2.10	1901	0.99	1915	0.860
1885-1888	1.95	1902	1.21	1916	1.103
1889	1.67	1903	1.24	1917	1.354
1890	2.09	1904	0.88	1918	1.598
1891	2.13	1905	0.94	1919	1.710
1892	2.11	1906	1.13	1920	2.020
1893	1.91	1907	1.11	1921	1.890
1894	1.73	1908	0.85	1922	1.760
1895	1.60	1909	0.813		
1896	1.57	1910	0.891		

TABLE VII.—PER CAPITA CONSUMPTION OF CEMENT.

Year	Barrels	Year	Barrels
1914	0.77	1919	0.77
1915	0.83	1920	0.86
1916	0.89	1921	0.87
1917	0.84	1922	1.06
1918	0.64		

CHAPTER II

THE NATURE AND COMPOSITION OF PORTLAND CEMENT

Portland cement may be defined as "the product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum."[1]

When the fine powder is mixed with water chemical action takes place, and a hard mass is formed. The change undergone by the cement mortar in passing from the plastic to the solid state is termed "setting." This usually requires but a few hours at most. On completion of the set a gradual increase in cohesive strength is experienced by the mass for some time, and the cement is said to "harden." Cements usually require from six months to a year to gain their full strength. Cement differs from lime in that it hardens while wet and does not depend upon the carbon dioxide of the air for its hardening. It is very insoluble in water and is adapted to use in moist places or under water where lime mortar would be useless.

Composition of Portland Cement

The composition of Portland cement may be considered from two viewpoints, that of the analyst and that of the physical chemist. The analyst concerns himself with the quantities of certain elementary compounds such as silica, alumina, lime, etc., which are present in cement, while the physical chemist determines the relation which these compounds bear to each other, their physical form, state of equilibrium, etc. Cement is such a complex substance that two lots having identically the same analysis, fineness, etc., may yet have quite different setting properties. This difference is due to a difference in the chemical structure of the

[1] Standard Specifications for Portland Cement, Amer. Soc. Test. Mat.

two cements. A study of the latter is therefore necessary if the behavior of cement is to be understood.

Turning our attention first to the analysis of cement and the composition of the material as shown by this, we find that the present state of the art of cement analysis is by no means as satisfactory as it might be, and expert and careful chemists do not always agree upon even the analysis of cement. After the careful work[1] done by two committees and one of the best chemists of the United States Geological Survey, it would seem as if the conditions for accurate work had been so fully established as to insure agreement among skillful chemists. That this is not so the following incident will show. Some years ago the author was associated with two prominent American chemists in the examination of some thirty samples of cement. The average results of the three sets of determinations are given below and demonstrate clearly how unsatisfactory is the present state of analytical chemistry.

Chemist	A	B	C	Variation between extremes
Lime	60.75	61.13	61.19	0.46
Silica	22.59	22.28	22.11	0.48
Alumina	6.88	7.56	8.59	1.71
Iron oxide	3.40	3.61	2.56	0.84
Magnesia	1.20	0.92	1.58	0.66
Sulphur trioxide	1.09	1.20	1.31	0.22
Loss on ignition	2.22	2.22	2.37	0.25

Substances Found in Cement

Whatever may be the nature of their combination with each other the essential elements of Portland cement are lime, silica,

[1] Richardson, Schaffer and Newberry—*J. Soc. Chem. Ind.*, **21**, 830 and 1216; *J. Am. Chem. Soc.*, **25**, 1180, and **26**, 995.
Meade, Newberry and McCready—*Cement and Eng. News*, Aug., 1904, *Chem. Eng.*, 1.
Hillebrand—*J. Am. Chem. Soc.*, **24**, 362.
Peckham—*J. Soc. Chem. Ind.*, **21**, 831, and *J. Am. Chem. Soc.*, **26**, 1636.
Blount—*J. Am. Chem. Soc.*, **26**, 995.
Gano—*Chem. Eng.*, **9**, 7.

and alumina. In the cements of commerce, iron replaces some alumina and magnesia some lime, since clays usually contain a considerable amount of the former, and limestones are rarely free from at least a few tenths of a per cent of the latter. Other elements which are found in one or the other or even both of the raw materials and which find their way into the final product are the alkalies, manganese, titanic acid, phosphoric acid, sulphuric acid and strontium. Sulphate of lime, either in the form of gypsum, $CaSO_4.2H_2O$, or of plaster of Paris $(CaSO_4)_2.H_2O$, is added to regulate the setting time, and carbon dioxide and water are absorbed from the air by the clinker, either before or after grinding. Of these elements, lime, silica, alumina, iron and sulphuric acid all exercise an important influence on the cement, and its properties will depend largely upon the relative amounts of these present. The alkalies, no doubt, if present in larger quantities, would affect to some degree at least the physical properties of cement, but in the small amounts found in American Portland cements the rôle they play is a very slight one. Table VIII gives the analyses of a larger number of American Portland cements from different parts of the country, and made from various raw materials.

Referring to Table VIII, we see that the chemical composition of American Portland cements which pass the standard specifications for soundness, setting time and tensile strength falls within the following limits:

	Per cent
Silica	19—25
Alumina	5— 9
Iron oxide	2— 4
Lime	60—64
Magnesia	1— 4
Sulphur trioxide	1— 2

The average is represented by the following:

	Per cent
Silica	22.0
Alumina	7.5
Iron oxide	2.5
Lime	62.0
Magnesia	2.5
Sulphur trioxide	1.5

TABLE VIII.—Analysis of American Portland Cements.
(Made by the author with the exception of those marked *.)

Made from	Where made	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss
Cement-rock and limestone	Nazareth, Pa.	19.92	2.28	7.52	62.48	3.19	0.52	0.66	1.51	1.46
	Nazareth, Pa.	21.14	2.30	6.94	63.24	3.26	0.36	0.51	1.12	1.24
	Bath, Pa	19.64	2.80	7.52	62.31	3.04	n. d.		1.60	1.48
	Alpha, N. J.	21.82	2.51	8.03	62.19	2.71	n. d.		1.02	1.05
	Northampton, Pa.	21.94	2.37	6.87	60.25	2.78	0.61	0.87	1.38	3.55
	Coplay, Pa.	22.26	2.10	5.36	63.32	3.81	n. d.		0.89	1.24
	Omrod, Pa.	22.20	2.27	6.69	62.61	3.00	0.32	0.61	1.32	1.56
	Martin's Creek, Pa.	20.32	2.50	7.12	62.94	3.38	n. d.		1.45	1.25
	Reading, Pa.	24.16	1.45	5.10	62.95	3.12	0.21	0.50	1.35	1.40
Limestone and clay roshale	Bay City, Mich	20.72	2.85	7.17	62.64	1.97	0.48	0.12	1.42	2.58
	Wellston, O.	21.84	5.05	6.77	62.66	0.80	n. d.		1.24	..
	Chanute, Kan	20.74	3.72	7.06	62.76	1.78	0.41	0.23	1.12	1.40
	Ada, Okla.	12.28	3.20	6.36	59.66	3.11	0.80	0.25	1.40	2.82
	*Glens Falls, N. Y.	21.50	10.50		63.50	1.80	0.40		1.50	n. d.
	Alsen, N. Y.	23.94	3.20	5.62	62.32	1.77	n. d.		0.90	1.68
	Fordwick, Va.	21.31	2.81	6.54	63.01	2.71	n. d.		1.42	2.01
	Davenport, Cal.	25.38	1.20	3.34	62.96	1.20	n. d.		0.35	4.58
	Cement, Cal.	22.34	3.30	7.00	60.72	1.30	n. d.		1.05	2.54
	*Baker, Wash.	24.63	8.56		62.88	1.60	n. d.		1.33	n. d.
	St. Louis, Mo	23.12	2.49	6.18	63.47	0.88	n. d.		1.34	1.81
	Demopolis, Ala	19.36	4.10	9.18	63.20	1.16	n. d.		1.18	1.12
	*Portland, Colo	21.88	2.85	7.14	64.94	trace	1.18		0.73	1.08
Marl and clay	*Middlebranch, O.	21.24	4.14	7.85	63.22	0.28	0.68		1.11	1.32
	*Coldwater, Mich	21.22	3.83	7.51	63.75	0.82	n. d.		1.58	1.02
	Sandusky, O	21.93	2.35	5.99	62.92	1.10	0.63	0.27	1.55	2.92
	*Bronson, Mich	22.90	3.60	6.80	63.90	0.70	1.10		0.40	0.60
	*Harper, O.	21.30	2.00	6.95	62.50	1.20	n. d.		0.98	4.62
	*Warners, N. Y.	22.04	3.41	6.45	60.92	3.53	n. d.		1.25	..
Limestone and blast furnace slag	Chicage, Ill.	22.41	2.51	8.12	62.01	1.68	n. d.		1.40	1.02
	Chicago, Ill.	23.06	2.88	8.16	62.10	1.88	0.36	0.58	1.57	..

The Lehigh Valley cements (made from argillaceous limestone) are characterized by high magnesia usually between 3 and 3.5 per cent, though occasionally as low as 2.5 per cent and as high as 5 per cent. They contain about 2.5 per cent iron oxide and about twice as much silica as iron oxide and alumina combined. In those cements from the western end of the deposit, this ratio is somewhat higher, however, owing to the fact that the cement-rock found here is higher in silica and also to the fact that the limestone used with this rock is silicious.

Most of the marl cements are low in magnesia, some of them containing as little as 0.5 per cent. Some of the Michigan marl cements are high in iron oxide, 3 to 4 per cent. This comes from the clay, or shale, however, and hence is also characteristic of some cements made from limestone and clay or shale.

The cements made from the Selma chalk at Demopolis, Ala., are high in iron and alumina, published analyses showing 12 to 14 per cent iron oxide and alumina and only about 2 per cent silica.

Early Studies of Cement

The scientific study of cements really began about the first quarter of the last century, and with the work of Collet-Descotils[1] and Vicat,[2] who showed that the hydraulic properties of cement were due to the fact that the burning of these materials converted the silica into a soluble form. The work of Vicat was especially noteworthy. Frémy[3] attributed the hardening to combined alumina, and A. Winkler[4] brought forward the theory that basic silicates were formed when cements were burned, and that these were hydrolysed when water was added, forming lime and hydrated less basic silicates.

Le Chatelier's Investigations

Le Chatelier[5] was the first chemist to apply to the study of cement the methods employed in petrography or the study of

[1] *Jour. des Mines*, 1813, **34**, 308.
[2] *Mortiers et Ciments Calcaires, Paris*, 1828.
[3] *Compt. Rend.*, 1856, **60**, 993.
[4] *J. Prakt. Chem.*, 1856, **67**, 44.
[5] Constitution of Hydraulic Mortars (Trans. by J. L. Mack), *Ann. des Mines*, 1887, p. 345.

rocks. In 1887 he published as his thesis for the degree of doctor of science a dissertation upon the "Experimental Study of the Constitution of Hydraulic Mortars," in which he propounded the theory that Portland cement was composed of two essential compounds, tricalcium silicate, $3CaO.SiO_2$, and tricalcium aluminate $3CaO.Al_2O_6$. He arrived at this conclusion after a long series of experiments, which consisted in examining thin sections of cement clinker under the polarizing microscope. He also made experiments upon the synthetic production of calcium silicates and aluminates by heating intimate mixtures of finely pulverized silica, alumina, and lime. He then examined into the hydraulic properties of the compounds so prepared. He, however, failed to prepare the tricalcium silicate directly by heating lime and silica, the result of the attempt being a mixture of lower silicates and lime, but gave it as his opinion that this compound could be prepared indirectly by heating together a mixture of fusible silicates and lime.

Assuming that three molecules of lime are united to one of silica to form the tricalcium silicate, that three molecules of lime are united to one of alumina to form the tricalcium aluminate, and that these two compounds are the essential ingredients of cement, Le Chatelier gives the following as the ratio between the lime and magnesia, the basic elements, and the silica and alumina, the acid elements in a good cement

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} < 3 \qquad (1)$$

and

$$\frac{CaO + MgO}{SiO_2 - Al_2O_3 - Fe_2O_3} > 3 \qquad (2)$$

Le Chatelier also states that (1) usually gives for a good cement from 2.5 to 2.7, and (2) from 3.5 to 4.

Ten years later, Messrs. Spencer B. and W. B. Newberry[1] confirmed the views of Le Chatelier so far as tricalcium silicate was concerned, but advanced the theory that the alumina was present as dicalcium aluminate, $2CaOAl_2O_3$. They prepared

[1] *J. Soc. Chem. Ind.*, **11**, 1035.

what they supposed to be silicates and aluminates of lime synthetically, just as did Le Chatelier, by heating together in a Fletcher gas furnace intimate mixtures of finely pulverized quartz and calcium carbonate, and of alumina and calcium carbonate in different molecular proportions. They then examined into the hardening and setting properties of the resulting compounds.

Their experiments led them to the following conclusions:

"*First.*—Lime may be combined with silica in the proportion of 3 molecules to 1, and still give a product of practically constant volume and good hardening properties, though hardening very slowly. With 3½ molecules of lime to 1 of silica the product is not sound, and cracks in water.

"*Second.*—Lime may be combined with alumina in the proportion of 2 molecules to 1, giving a product which sets quickly, but shows constant volume and good hardening properties. With 2½ molecules of lime to 1 of alumina the product is not sound."

These experimenters made an error quite common with all earlier investigators, assuming that the preparation of a compound which was "sound" or "volume constant" was proof that this compound existed in cement and conversely that if the material was unsound it did not exist in cement. The fallacy of this reasoning will be evident later on and led the Newberrys into the wrong conclusion that alumina was present in cement as dicalcium aluminate. Their work advanced no new tenable theories as to the composition of cement and are principally of importance as the effort of American chemists, actually engaged in the manufacture of cement, to devise a scientific basis for proportioning the raw materials. Their formula is quite generally referred to in the literature of cement and was accepted by mill chemists as reliable.

Newberry's Formula

The formula for the tricalcium silicate, $3CaO.SiO_2$, corresponds to 2.8 parts by weight of lime to 1 part of silica, and the formula for the dicalcium aluminate, $2CaO.Al_5O_3$, corresponds to 1.1 parts of lime to 1 of alumina. From this the following formula is given as representing the maximum of lime which

should be present in a correctly balanced Portland cement; per cent lime = per cent silica × 2.8 + per cent alumina × 1.1.

They found that cement prepared synthetically with lime, alumina, and silica proportioned according to the above formula gave good results, whereas that prepared by Le Chatelier's formula was unsound, showing the lime to be in excess.

Törnebohm's Investigations

Törnebohm,[1] a Swedish investigator, checked the microscopic work of Le Chatelier and identified in Portland cement four distinct mineral constituents which he called *Alit, Belit, Felit* and *Celit*, and described as follows:[2]—

"Alit is the preponderating element and consists of colorless crystals of rather strong refractive power, but of weak double refraction. By this he means that Alit in polarized light between crossed Nicol prisms has insufficient optical activity to produce more than weak interference colors of a bluish gray order.

"Celit is recognized by its deep color, brownish orange. It fills the interstices between the other constituents and eventually forms the magma or liquid of lowest freezing point out of which the Alit is separated. It is strongly double refractive, that is to say, gives brilliant colors when examined between crossed Nicol prisms.

"Belit is recognized by its dirty green and somewhat muddy color and by its brilliant interference colors. It is bi-axial and of high index of refraction. It forms small round grains of no recognized crystalline character.

"Felit is colorless. Its index of refraction is nearly the same as that of Belit and it is strongly double refractive. It occurs in the form of round grains, often in elongated form, but without crystalline outline. Felit may be entirely wanting.

"Besides these minerals an amorphous isotropic mass was detected by Törnebohm and Le Chatelier. It is called isotropic because it has no effect upon polarized light. It has a very high refractive index.

[1] Kongreb des intern verb. für material prüff Stokholm, 1897.
[2] Richardson—Papers Asso. Port. Cem. Mfgs., June 15, 1904.

"Törnebohm adds the important fact that a cement 4 per cent richer in lime than usual consists almost entirely of Alit and Celit."

Richardson's Work

Clifford Richardson, an American chemist, in two papers, read before the Association of American Portland Cement Manufacturers, June 15 and December 14, 1904, described the results of a thorough and exhaustive microscopic study of Portland cement clinker. As the result of this investigation he again advanced the theory first brought forward by Winkler[1] in 1858, I believe, that Portland cement clinker is a solid solution. This paper was one of the first attempts to explain the properties of cement along the lines of physical chemistry, and the investigations which led up to it were very thorough. Richardson prepared many synthetic silicates and aluminates and determined their optical properties, hydraulic value and physical characteristics.

Richardson next prepared clinkers of pure silica, alumina and lime in the proportions met with in the industrial product and thin sections of these clinkers were then examined under the microscope. As the result of this investigation, he gave as his opinion that the Alit of Törnebohm, the essential constituent of Portland cement, was a solid solution of tricalcium silicate, $SiO_2 3CaO$, in tricalcium aluminate, $Al_2O_3 3CaO$, and that Celit was a solid solution of one dicalcium compound in the other.

Richardson also concluded that the setting of Portland cement is almost entirely due to the decomposition of the Alit, examination showing the Celit to be almost unattacked.

Richardson also concluded as did most of his contemporaries that the hardening of cement was due to the formation of a net work of interlacing crystals of calcium hydrate. More recent investigation shows that he was wrong in this theory and also in assuming that Alit and Celit were solid solutions.

Researches of Day, Shepard and Rankin

About this time the chemists of the Geophysical Laboratory of the Carnegie Institute began their investigations on the com-

[1] *Dingler's polyt. Jour.*, **175**, 208.

position of cement, and these researches, together with those made later at the U. S. Bureau of Standards, have contributed largely to our present theory as to the chemistry of cement. The first paper[1] from the former laboratory appeared in 1906. The authors of this, Day and Shepard, stated that they had been unable to prepare tricalcium silicate directly by simply heating a mixture of silica and lime together and that the compound so called, even as prepared by others, was merely a mixture of lime and calcium orthosilicate (dicalcium silicate). The proofs which they gave of this were quite conclusive and are generally accepted.

Following up this work, however, Shepard and Rankin found that by prolonged heating at a temperature below 1,900° C. of a mixture of the finely divided oxides in proper proportions, tricalcium silicate could be produced, but that the production of the pure compound was very difficult owing to the high temperature required. They found, however, that if a small amount of alumina is present the combination is more rapid and takes place at a lower temperature, etc. This work was then followed up by a very thorough investigation of cement clinker in which Rankin, Bates, Klein, Phillips, Wright and other chemists of the above laboratories took a leading part. Before going on to the conclusion of these later investigations, however, it may be well to explain certain terms and diagrams used by physical chemists in illustrating the composition of cement and similar materials.

The Use of Triangular Diagrams

A triangular diagram is often employed for illustrating the composition of cement clinker. This method of representing a system of three components was proposed by Gibbs[2] and improved by Roozeboom.[3] It consists in employing an equilateral triangle the length of whose side is made equal to one hundred, Fig. 1. The sum of the percentage amounts of the three components is therefore represented by a side. The apices of the triangle represent the pure substances and hence in the CaO-

[1] *Am. Chem. Soc,*. **28**, 1089.
[2] *Trans. Conn. Academy*, 1876, **3**, 176.
[3] *Zeitschr. Physikal Chem.*, 1894, **15**, 147.
See also "The Phase Rule," by Alex Findlay, London, 1903.

Al_2O_3-SiO_2 series the three oxides. Points on the side represent the binary compounds, that is compounds composed of the two oxides at the ends of the side such as $3CaO.SiO_2$, $3CaO.Al_2O_3$, etc. Points on the interior of the triangle represent the composition of a ternary mixture, or a mixture of the three oxides. In this case, the composition is determined by the distance of the point from the three sides measured in a direction parallel to

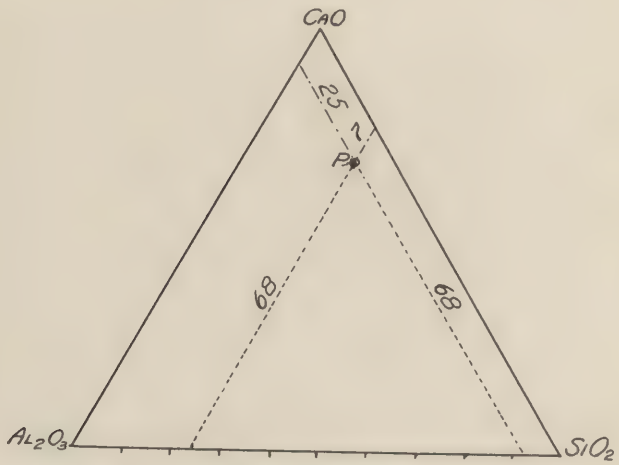


Fig. 1.—Triangular Diagram of a Ternary System.

the sides of the triangle. To illustrate, we may take the converse of this and suppose that we have a mixture consisting of silica 25 per cent, alumina 7 per cent and lime 68 per cent. Referring to Fig. 1 we first measure off 7 along the side Al_2O_3-SiO_2 from the SiO_2 apex, then 25 on this same side from the Al_2O_3 apex, and draw lines through these points parallel to the nearest sides. These lines will meet at a point "P" which represents the composition of this ternary mixture. The distance of the point "P" from the three sides of the triangle when measured in directions parallel to the sides is equal to 7, 25 and 68 respectively. Manifestly if we knew the position of any point in the triangle we can find the composition this represents by measuring the distance to the sides along a direction parallel to the latter.

In each instance remember that the distance in a direction *away* from the apex gives the percentage of the compound at the apex, etc.

The Ternary System CaO-Al_2O_3-SiO_2

Practically all investigators agree that the essential elements in Portland cement are silica, alumina and lime, and that the other compounds, while they may exert some influence on the properties of cement, are not themselves of any importance and are merely present as impurities. The problem therefore is that of determining the properties of these three compounds when associated together. This work Rankin[1] undertook. He de-

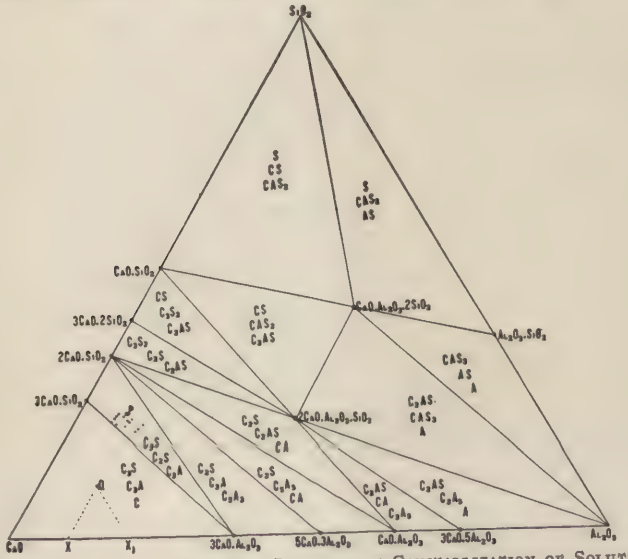


FIG. 2.—DIAGRAM TO SHOW FINAL PRODUCTS OF CRYSTALLIZATION OF SOLUTIONS CaO, Al_2O_3 AND SiO_2.

Within each small triangle symbols, C = CaO; A = Al_2O_3; S = SiO_2, are used to simplify the designation of the compounds. Thus: $3CaO.SiO_2 = C_3S$; $5CaO.3Al_2O_3 = C_5A_3$; etc.

termined and investigated all compounds formed when any mixture of these three oxides is heated at a high temperature and collected the necessary data to plot the relation between the three oxides. His complete diagram is given in Fig. 2. As Le Chat-

[1] *Am. Jour. Sci.*, 1915, **39**, 1-79.

elier,, Richardson, Bates and others have shown that only a few compounds are present in cement, however, we are interested only in the small portion of this triangle in which the more basic compounds lie and Fig. 3 is an enlargement of this. By referring to this latter diagram, it will be seen that if we join the points on the left side representing $3CaO.Al_2O_3$ and $2CaO.SiO_2$ with the point on the lower side representing $3CaO.Al_2O_3$, and the point $2CaO.SiO_2$ with the point $5CaO.2Al_2O_3$ by lines we will form three small irregular triangles. Each of these triangles repre-

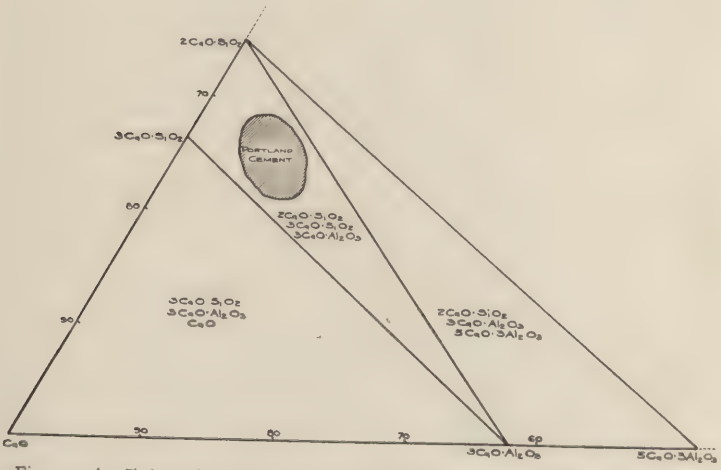


Fig. 3.—An Enlarged Portion of the Ternary Diagram in the Region Occupied by Portland Cement.

sents all possible mixtures of these three compounds whose symbols are at the apices of the triangle. Though a group of three compounds can exist only in a given triangle yet any of these three compounds may be found in a number of adjacent triangles as will be seen. Points which fall on the sides of the triangle represent binary mixtures of the two components at each end of the line, etc.

Any point whose composition falls in one of these three triangles will be a mixture of the three compounds shown at the apices of this small triangle. Thus any point within the tri-

angle $2CaO.SiO_2$-$3CaO.SiO_2$-$3CaO.Al_2O_3$ will be a mixture of these three compounds. This supposes that the compound is in a state of equilibrium, which is another way of saying that combination shall be complete. If the mixture is not in a state of equilibrium, we will have some of the compounds from the adjoining triangles. If the location of the point is near the line $3CaO.SiO_2$-$3CaO.Al_2O_3$, we shall have more $3CaO.SiO_2$ present than $2CaO.SiO_2$, and CaO present if the equilibrium is not quite complete. Conversely, if the point is near the line $2CaO.SiO_2$-$3CaO.SiO_2$, the $2CaO.SiO_2$ will be in excess, and $5CaO.2Al_2O_3$ present if equilibrium has not been entirely established. The symbols within the triangles indicate the compounds present when the point lies within this triangle and perfect equilibrium is attained.

If commercial Portland cements are plotted, it will be found that they lie wholly within the triangle $3CaO.SiO_2$-$2CaO.SiO_2$-$3CaO.Al_2O_3$ and hence are composed almost entirely of these three compounds. As commercial cements are not in a state of perfect equilibrium some CaO and $5CaO.2Al_2O_3$ are also present in small amounts, the amounts varying with the completeness with which equilibrium has been established by fine grinding of the raw materials, temperature of the kiln and the duration of burning at this temperature.

The Compounds in Cement

All of these compounds of lime and silica, and of lime and alumina have very definite optical properties and these have been measured very carefully by Drs. Rankin and Wright[1] and their associates. After carefully determining the optical characteristics of these compounds, they were able to identify them in commercial Portland cement clinker. They found that even in the presence of magnesia, iron oxides and the other impurities found in clinker, that these characteristics persisted and that they could definitely identify five compounds in commercial Portland cement clinker. These compounds are CaO, $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$. These substances are pres-

[1] *Amer. Journ. Sci.*, 1915, **39**, 1-79.

ent as a homogeneous mixture and not as a solid solution. Alit is composed presumably of a mixture of tricalcium silicate and tricalcium aluminate, while Belit is the fusion or melt in which these compounds are formed. Rankin made a very careful examination of these compounds mentioned above to determine their physical properties and the conditions under which they are formed, and his results are given below.[1]

The component lime, CaO, is formed by burning $CaCO_3$ to drive off CO_2; it is stable at its melting point which is 2,570° C.

The compound dicalcium silicate, $2CaO.SiO_2$, (by weight CaO 65 per cent, SiO_2 35 per cent) is easily formed by crystallizing a melt of the composition $2CaO$ to $1SiO_2$ (by weight CaO 65 per cent, SiO_2, 35 per cent), though it will also form at temperatures much below its melting point which is 2,130° C. It occurs in four forms: α, which is stable between 2,130-1,420°; β, which is stable between 1,420-675°; γ, which is stable below 675°; and β', which is unstable or monotropic and is found occasionally in charges rapidly cooled from a temperature of about 1,400°. The change β to γ at a temperature of 675° is accompanied by a volume change of about 10 per cent, which shatters the crystals; this is the phenomenon commonly known as "dusting." Of these four forms of $2CaO.SiO_2$, the high temperature forms α and β are the more common in Portland cement. Bates finds that $2CaO.SiO_2$ is found in well-burned commercial clinkers largely as the β form. The γ form is not found to any extent except in underburned clinkers which "dusted" on cooling.

The compound $5CaO.3Al_2O_3$ (by weight CaO 47.78 per cent, Al_2O_3 52.22 per cent)is the most easily fusible; it melts at 1,455° and crystallizes again readily from the melt. It is also found in a second form which is monotropic and generally occurs in melts that have cooled rather rapidly, though the precise conditions under which it does form have not been ascertained. The stable form of this compound is, according to Bates, the more common in commercial cement clinker.

The compound tricalcium aluminate $3CaO.Al_2O_3$, (by weight CaO 62.22 per cent, Al_2O_3 37.78 per cent) has no stable melting

[1] *Journ. Ind. and Eng. Chem.*, 1915, **7**, 466.

point; at a temperature of 1,535° C. it dissociates into CaO and liquid wherefore it is exceedingly difficult to obtain free from admixture of free lime and $5CaO.3Al_2O_3$. If a well-mixed charge of the oxides in the proportion 3CaO (as $CaCO_3$): Al_2O_3 is fused and examined under the microscope, it is seen to consist largely of $3CaO.Al_2O_3$, but to contain also some free CaO and $5CaO.3Al_2O_3$. If, however, the mixed oxides are not fused but are held for several hours at a temperature somewhat below 1,535° (*i. e.*, the dissociation point of this compound)—say 1,400°—the charge becomes homogeneous and contains only $3CaO.Al_2O_3$. This compound has been found in but one form.

The compound tricalcium silicate, $3CaO.SiO_2$ (by weight CaO 73.59 per cent, SiO_2 26.41 per cent) also has no melting point, dissociating at about 1,900° into free CaO and $2CaO.SiO_2$, but this dissociation differs in one respect from that of $3CaO.Al_2O_3$ in that the charge remains solid because 1,900° is still about 100° below the temperature at which melt (liquid) appears in this case. It can be obtained in the pure state by a procedure analogous to that for $3CaO.Al_2O_3$, namely by prolonged heating of a mixture of the oxides in the proper proportions at a temperature somewhat below 1,900°. The formation of this compound pure is very difficut, owing to the high temperature required. The compound $3CaO.SiO_2$ occurs in but one form; on fusion it is transformed completely into CaO and $2CaO.SiO_2$. As was to be expected; it was found by Bates that the relative amounts of this compound in commercial clinker increased with the temperature of burning.

The Formation of Cement Clinker

Having considered the formation of each pure compound separately, let us now take up the mode and order of formation of the four compounds in the burning of cement clinker made up from the pure oxides CaO (as $CaCO_3$), Al_2O_3 and SiO_2 in the proper proportions. When such a mixture is heated, the first change is the evolution of the CO_2; the lime then unites with the other components to form the compounds which form most readily, $5CaO.3Al_2O_3$ and $2CaO.SiO_2$; probably in the order

given, since the former melts at a lower temperature than the latter. These two compounds next unite in part with more lime and the compounds $3CaO.SiO_2$ and $3CaO.Al_2O_3$ appear. The formation of the last two compounds would go on very slowly in mixtures of these two compounds only but is materially facilitated by the fact that a portion of the charge has already melted and promotes reaction by acting as a flux or solvent. In commercial cements, this fluxing action is increased by the presence of the iron oxide and the alkalies which lower still further the melting point of the solvent. The temperature at which this flux first appears with pure materials is 1,355° C., the eutectic temperature for the three compounds, $2CaO.SiO_2$, $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$. As the temperature of burning gradually rises above 1,335°, the relative amount of flux increases and the rate of formation of $3CaO.Al_2O_3$ and $3CaO.SiO_2$ increases correspondingly. At a temperature somewhat above 1,335° (the exact temperature depending on the original composition), the compound $5CaO.3Al_2O_3$ will have completely melted in the flux and the formation of the compound $3CaO.Al_2O_3$ will be completed. The substances present as crystals at this stage are $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$ and free CaO. If the burning were stopped at this stage the cement would be "unsound" due to the free lime. If the heating is continued, the $3CaO.SiO_2$ rapidly increases in amount, due to combination of $2CaO.SiO_2$ with CaO, while the amount of solid $2CaO.SiO_2$, CaO and $3CaO.Al_2O_3$ are all decreasing, the $2CaO.SiO_2$ partially by combination with CaO and partially by dissolving along with $3CaO.Al_2O_3$ in the flux. At a temperature of about 1,475° C., the $3CaO.Al_2O_3$ will all have dissolved in the flux and most of the CaO will have combined with $2CaO.SiO_2$ to form $3CaO.SiO_2$, so that the crystalline substances now present in the flux are $3CaO.SiO_2$, $2CaO.SiO_2$ and a trace of CaO. As the temperature is raised still further each of these crystalline compounds will gradually disappear, but it is possible to state which of these crystalline phases will be the last to dissolve only if the original composition of the charge is known. In any case the temperature of complete melting will be about 1,900°

and if such a charge is cooled the final product of crystallization will consist largely of $3CaO.SiO_2$, $2CaO.SiO_2$ and $3CaO.Al_2O_3$.

In cement burning the temperature is never carried to that necessary to fuse or flux the entire mass. Rankin states that with white cement good results are obtained with 30 per cent melted and 70 per cent solid crystalline material .

Experiments of Bates and Phillips

Following up the work of Rankin, Bates and Phillips[1] investigated the properties of various compounds existing in cement when treated with water, both alone and in mixtures. Their work consisted in the preparation of the pure compounds themselves and also the burning of cements of certain definite compositions, corresponding respectively to a low lime-high silica clinker, a normal clinker, and a high lime-low silica clinker.

Their investigations show that the important elements of cement so far as the hardening goes are the tricalcium silicate and the dicalcium silicate and that alumina compounds are needed only as a flux and are of themselves of doubtful value aside from this.

According to this investigation, tricalcium aluminate hydrates almost immediately on adding water with the evolution of so much heat that the mixture boils. In fact, the reaction is so violent that it is difficult to properly hydrate the compound. Much more water is required than for cement. This compound makes a very plastic mass which may be wetted and worked up again after it has apparently set. It gains practically all its strength within 24 hours but is too weak and sets too rapidly to be of commercial use by itself.

Dicalcium silicate has apparently no setting properties in the ordinary sense of the word, but it does hydrate very slowly. This hydration is most marked after seven days. At early periods, the compound has hardly any strength. Bates attributes the slow hardening of cements at periods beyond 28 days to the action of this compound and states that it then becomes equal to tricalcium silicate in strength. Dicalcium silicate, however, sets and hardens too slowly for commercial use alone.

[1] Tech. Paper No. 78, U. S. Bureau of Standards.

If tricalcium aluminate is added to dicalcium silicate, the mixture sets very quickly with the evolution of heat. Addition of plaster of Paris fails to slow the set and the pats are unsound in steam.

Tricalcium silicate has all the properties of cement except a slightly inferior plasticity. At early periods (seven days), it is the strongest of the three compounds. The addition of 3 per cent of gypsum to tricalcium silicate gives it plasticity and quickens its set. Tricalcium silicate gains its full strength before seven days.

The addition of tricalcium aluminate to tricalcium silicate increases its plasticity but decreases its strength. The mixture gives off heat and is quicker setting than the tricalcium silicate alone. If plaster is added to the mixture of the two compounds, it reduces the amount of heat evolved and slows the initial set. Mortar which has set can not be regauged with water to any extent.

A mixture of tricalcium silicate and dicalcium silicate resembles cement except that it works more sandy. The addition of plaster increases the plasticity and reduces the time of setting. If on the other hand, tricalcium aluminate is also added, the mixture has a flash set, heat being evolved. The aluminate increases the plasticity. If plaster is added to the three compounds it reduces the heat evolved, increases the initial set, reduces the final set and makes a more plastic mortar. Mixtures of tricalcium silicate and dicalcium silicate pass the steam test but those in which tricalcium aluminate is used do not.

Setting and Hardening of Cement

Nearly all of the early investigators of the composition of Portland cement contended that the hardening of cement was due to the formation of a net work of hydrated crystals of calcium hydrate which crystallized out of a saturated solution of this compound. These chemists held that when water is added to cement, free lime is liberated and that this at the moment it is liberated is in solution in the water as calcium hydrate. Owing, however, to the rapidity with which the free lime is formed, the water soon becomes supersaturated with calcium hydrate and

the latter crystallizes out in a net-work of crystals, which bind the particles of undecomposed cement together. It was also generally contended that the initial set is due to the aluminates, while the subsequent hardening is due to the slower reaction of the silicates.

Michaëlis[1] about 1893 suggested that calcareous hydraulic cements owe their hardening to the formation of colloidal calcium hydrosilicate. This theory did not gain much support, however, until quite recently when owing to the growth of interest in colloidal chemistry, the attention of the physical chemist has been turned to the properties of this remarkable series of compounds. Investigations made along the latter lines within the past decade now seem to confirm the theory of Michaëlis.

The term "colloid" as now applied can be taken as comprising everything formerly known as "amorphous," the latter in turn meaning not crystalline.[2] The term colloidal is from the French word meaning glue. Familiar examples of colloids are starch, gelatine, glue, gum, albumin, dextrin, etc. These organic substances are not the only colloids, however. Most analysts are familiar with the gelatinous way in which silica precipitates when acid is added to a soluble silicate such as cement or alumina when ammonia is added to an alumina salt in solution. Hydrous silicic acid and hydrous alumina are both examples of mineral colloids.

In the case of Portland cement, insoluble colloidal precipitates are formed by the action of the lime in solution on the silica and alumina in the cement forming a jelly-like mass, having very much the properties of glue. As the water is absorbed either by further chemical reaction or by drying out, these colloids become hard and dense and attain considerable mechanical strength.

A very interesting paper by F. Bluementhal[3] sums up very well the modern theory of the hardening of Portland cement. This writer states that when water is added to Portland cement the

[1] *Chemiker Zeit.*, (1893) **17**, 982.

[2] This definition of colloidal is probably not in accord with the latest developments of colloidal chemistry and is here used in a popular rather than a strictly chemical sense.

[3] English translation by W. Michaelis, *Cem. and Eng. News*, 1914, p. 270.

following products are formed. (1) Small hexagonal plate crystals composed of tricalcium aluminate. (2) Fine needle crystals of monocalcium silicate. (3) A colloidal mass of monocalcium silicate. (4) Large hexagonal crystals of calcium hydrate. These latter, however, contribute only indirectly to the hardening. Iron oxide may take part in the process of hydration by forming with the silica ferric silicate, or with lime tricalcium ferrite.

These compounds do not, of course, exist in the calcined clinker but are formed after previous decomposition of the compounds in the clinker by the water.

The hydration of cement takes place in two phases and setting and hardening may be considered as distinct stages in the chemical reaction which occurs when water is added to cement. The setting of the cement is a process of crystallizattion brought about by the formation of plate crystals of tricalcium aluminate and needle crystals of monocalcium silicate. This action is quite analogous to the setting of gypsum where the strength is conferred by the formation of crystals of hydrated calcium sulphate.

The hardening process on the other hand is due to an entirely different cause, namely, formation of a colloidal mass consisting of monocalcium silicate which cements the crystals in a mass of mineral glue. These colloids continue to form as long as calcium oxide, soluble silica and water are available.

From the paper[1] by Bates and Phillips referred to previously it appears that the dicalcium silicate hydrates to a very granular porous mass which allows of ready egress of solution and, while it is chemically more resistant to the action of solution than the tricalcium silicate, yet it furnishes a greater number of voids in which salts may crystallize out of solution and it is consequently very little able to resist the mechanical action of the freezing out (crystallization) of salts from solution.

The hydrated tricalcium silicate with its very dense structure composed of gelatinous (colloidal) silicate interspersed with crystals of lime hydrate is probably very susceptible to strains produced by alternate wettings and dryings, colloidal material of

[1] Technical Paper No. 78, U. S. Bureau Standards.

this kind being subject to considerable volume change from slight moisture changes. Arguing from this, these writers then suggest that the composition of cement should be along lines which would not produce a great preponderance of either silicate. This would give a not too dense hydrated material, gaining strength at later periods. A lesser amount of tricalcium silicate would furnish the desired early strength and also overcome the excessive porosity of the dicalcium silicate.

Effect of Theory upon Practice

It will be seen that during the last thirty years several quite distinct theories have been held as to the composition, setting and hardening of Portland cement, and we would expect these changes of theory to have some influence upon the practical manufacture of cement and the ultimate composition of the commercial product. This is not the case, however, and the effect of a change of theory upon practical cement making has been small.

The author recently went over some old note books and made an average of analyses of cement from the Lehigh district made prior to 1900, and compared this with an average of some fifty-odd analyses available of cement from the same district made during the past three years. In each case a number of brands were represented. The close agreement between the two averages is noticeable, as the following will show.

	1896-1900	1920-1923
Silica	21.80	21.72
Alumina	7.40	7.08
Iron oxide	2.48	2.54
Lime	62.45	62.20
Magnesia	2.86	3.84
Sulphur trioxide	1.54	1.60

It will be noted that the greatest difference is in the percentage of magnesia. This increase in the last twenty years is due to the change in specifications which now allow 5 per cent, whereas in 1896 only 3 per cent was permitted.

It must not be supposed from the foregoing, however, that American cements are not better to-day than they were ten years

ago, for in fact they are on an average much better, but this progress has been due to improved mechanical appliances rather than to any new ideas of how to make Portland cement, brought about by changes of our theory as to what the product really is. Nearly all investigators who attempted to prepare cement of varying composition called attention to the importance of fine grinding of the raw materials, but most mill chemists who were at all observant had previously noticed the relation between the fineness of the raw materials and "constancy of volume" of the resulting product. Great improvements have been made in recent years in grinding machinery. It is now possible to not only grind the raw materials much finer than formerly, but also to do this much more economically. The grinding of the raw materials to the point where the introduction of these latter into the kiln at a fineness of from 95 to 98 per cent passing the No. 100 sieve is now commercially practicable.

The rotary kiln also enabled the American manufacturer to improve considerably his product, as this kiln burns very uniformly when properly handled and no sorting of the clinker is necessary.

In spite of the uncertainty as to the constitution of Portland cement, the general influence of chemical composition upon physical properties is well understood among cement technologists; but this knowledge must be credited to practical experience rather than scientific theorizing. The controlling of the composition of the cement is nearly all of it done by rule of thumb methods, and each chemist employs the formula which practical experience has taught him best suits his conditions. The difference in raw materials and manufacturing conditions no doubt makes this necessary.

Lime

Most American cements, which meet standard specifications, contain, when freshly made, from 60 to 63.5 per cent lime. Since cements absorb water and carbon dioxide on exposure to air, the percentage of lime and also of all other elements, except the two absorbed, is lowered by the seasoning or storage of the

cement. In comparing the analyses of two cements, therefore, the amount of loss on ignition should always be considered, as a cement containing 63 per cent lime when fresh may contain 62 per cent or even less after exposure to air for a month.

Instead of comparing two cements by means of their analyses the better way is to determine their respective *"hydraulic indices"* or the reverse of this, which the author terms *"lime ratio."* The hydraulic index is generally understood to mean the ratio between the silica and alumina on the one hand and the lime on the other or expressed mathematically:—

$$\textit{Hydraulic index} = \frac{\%\ \text{silica} + \%\ \text{alumina}}{\%\ \text{lime}}.$$

The author's lime ratio is the reverse of this and takes into consideration the iron oxide also.

$$\textit{Lime ratio} = \frac{\%\ \text{lime}}{\%\ \text{silica} + \%\ \text{alumina} + \%\ \text{iron}}.$$

The amount of lime a cement may contain is dependent upon both factory conditions and the relative amount of silica to iron and alumina present. The maximum of lime is usually controlled by the "soundness tests" (which are now, in America, the boiling and steaming of small pats of neat cement for five hours). The minimum of lime is determined by the setting time of the cement, which must be such that the cement does not get its initial set in less than forty-five minutes, and also the strength which should be at least 200 pounds with sand per square inch.

Over-limed cements are "unsound," that is, in time concrete made from them will disintegrate and crumble or crack. Cements which are high in lime without being unsound are slow setting but harden rapidly, sometimes reaching their maximum strength in as short a period as seven days. Such cements, when subjected to tension tests, usually show retrogression as the test pieces grow older, but, when subjected to compression tests, show an increase of strength with age. This is due to the fact that high lime cements become very brittle on hardening, hence when they are tested in the ordinary manner more or less distortion is met with, owing to the shortness of the test piece,

and the briquette is snapped off, as it were, and not really pulled apart. Provided a cement is sound there is nothing in the theory so tenaciously held to by the school of engineers and chemists who borrow their ideas from the text-books of the past generation, that a cement must show a progressive gain. A cement which gets its strength promptly is certainly much better adapted to modern building conditions than one which requires a long period to reach the same point. With such a cement, forms can be promptly removed and it is also suited to work in cold weather, such as in thin partitions and floors, where slower hardening cement would be impracticable, owing to the length of time during which it is necessary to protect the work from the weather.

Cements low in lime usually contain clay in excess, for sufficient lime was not originally present in the raw material to change all the clay to silicates and aluminates. This excess of clay, of course, is devoid of cementing qualities and may be looked upon as just so much foreign matter. Though it will not cause the cement to fall to pieces subsequently, it takes away from its strength because in its place should be cement. Low lime cements are apt to be "quick-setting." Hence, one of the remedies for "quick-setting" cement is to increase the lime content of the raw mixture. For this reason high alumina cements often contain more lime than those low in alumina, in spite of the fact that alumina combines with less lime than does silica.

The amount of lime a cement will safely carry is dependent on the relative amounts of silica and alumina present and also on the care with which a cement is made. Practically all American cements fall between two limits, *i. e.*, the ratio of the lime to the silica, iron and alumina together should not exceed 2.1 : 1 nor be less than 1.9 : 1. To make a sound cement having the first ratio the raw materials must be well mixed and very finely ground. Such a cement will be much stronger, however, than one having the lower ratio.

Anything which will promote the combination or solution of the lime during burning will promote soundness. Thus the finer the raw materials are ground the more surface of contact between the acid and basic elements exists, hence fine grinding of

the raw materials is probably the most important requisite for the making of a sound cement. It is, of course, essential that the burning should be carried out at the proper temperature and be of sufficient duration to promote combination and solution. The greatest advance in the manufacture of Portland cement from the standpoint of quality has been in the introduction of more efficient grinding machinery, allowing the finer grinding of the raw materials and hence the manufacture of high limed, sound cements of great strength.

The percentage of lime to be carried at any works is usually controlled by two things, the "setting time" and the "soundness." There must be enough lime present to keep the cement from being quick-setting, either when made or after seasoning, and there must not be so much lime present that the cement will not pass the soundness tests.

It should also be borne in mind that, if equilibrium has been attained, the higher the lime the more tricalcium silicate will be present, while low lime cements will contain a preponderance of the dicalcium silicate.

Silica and Alumina

Silica and alumina, the other essential constituents in Portland cement, have also an equally important bearing on the strength. From the nature of things, cements high in alumina are low in silica and those low in alumina are high in silica. Cements usually contain 19 to 25 per cent silica and from 5 to 9 per cent alumina. High silica cements are usually slow-setting and of good tensile strength. They harden also slowly and usually show a progressive gain. High alumina cements are apt to be quick-setting and indeed if much more than 10 per cent alumina is present the cement is almost sure to be quick-setting even with the addition of sulphates. High alumina cements also are quick hardeners and consequently cements containing from 7½ to 10 per cent alumina show high seven-day tests. Cements should contain at least 2.5 times as much silica as alumina. This ratio

between the silica and the alumina the author calls the *index of activity*, or

$$\textit{Index of activity} = \frac{\%\ \text{silica}}{\%\ \text{alumina}}.$$

This index should lie between 2.5 and 5. Cements with an index of activity of less than 2.5 are apt to be quick-setting or else to become quick-setting on exposure to air. In order to offset this tendency to set quickly on the part of high alumina cements, it is necessary to make them relatively higher limed than those containing moderate percentages of alumina. The high lime content gives slow-setting properties which offset the quick-setting ones due to high alumina. This is necessary in spite of the fact that silica combines with more lime than does alumina. If we assume both the silica and the alumina to be present as tricalcium silicates and tricalcium aluminates, then silica combines with 1.7 times as much lime as alumina. On the other hand alumina increases the fluidity of the magma, and hence makes the cement more easily burned. Indeed cements high in alumina are hard to burn properly, owing to the fusibility of the calcium aluminate. This causes agglomeration and sticking together of the clinker in the hot zone of the kiln preventing uniform burning.

Cements with an index of activity of more than 5 are usually very hard to burn. They are slow-setting and also slow hardeners. Their early strength is often low but ultimately they obtain as great strength as other cements. There are a number of high silica cements on the American market which have great difficulty in meeting standard specifications as to seven-day strength.

Alumina probably adds to the plasticity of the cement. Bates concludes alumina has no value in cement except as a flux. If this is so, it should be possible to replace alumina by some other compound forming with lime bodies of low melting point, such as iron oxide for example. Experience, however, does not bear him out, at least so far as replacing alumina by iron oxide goes, since high iron cements have quite different properties from those high in alumina.

Ferric Oxide

According to Le Chatelier, ferric oxide and calcium carbonate on burning yield products which slake with water and possess no hydraulic properties. Schott, however, prepared cement containing only lime, silica and ferric oxide, which showed excellent hardening qualities, and therefore concluded that alumina could be completely replaced by ferric oxide without diminishing in any way the hydraulic properties of cement. S. B. and W. B. Newberry from their researches concluded that ferric oxide and alumina act in a similar manner in promoting the combination of silica and lime. Zulkowsky also made experiments along this line and his conclusions agree with those of Schott and Newberry, and it is now generally agreed that the iron oxide in the cement mixture acts as a flux and promotes the combination of the silica and the lime.

Mixtures of silica, alumina, and lime, in the proportions usually found in cement, are extremely hard to burn. The replacement of part of the alumina by iron, however, greatly lowers the temperature of burning. One of the cures for unsound cement is therefore found in the replacement of clays high in alumina by those high in iron. As iron does not seem to make cement quick-setting, iron may be made to replace alumina to advantage in many instances. In mixtures high in silica and consequently hard to burn, the addition of some soft iron ore, such as brown hematite, to the mix would lower the temperature at which clinkering takes place and make it easier to produce a sound cement.

Iron on the other hand makes a very hard clinker and high iron cements have been found very hard to pulverize, hence in most cases it will be found more economical to grind the raw materials finer than to add iron ore and produce harder grinding clinker. High silica clinkers are relatively speaking soft.

The color of cement is also due to iron. Cement made from materials containing no iron is perfectly white. It requires a higher temperature to burn, but when properly clinkered possesses all the setting and hardening properties of Portland cement. White Portland cements are now made at a number of

places in this country. Below are given some analyses of commercial white Portland cement:

ANALYSES OF WHITE PORTLAND CEMENT.

Brand	Medusa Per cent	Atlas Per cent	Berkohire Per cent
Silica	23.56	24.66	24.04
Iron oxide	0.32	0.38	0.35
Alumina	5.66	5.60	6.21
Lime	64.12	61.87	64.98
Magnesia	1.54	0.90	1.42
Sulphur trioxide	1.50	1.51	1.54
Loss on ignition	2.92	3.84	1.00

These white cements have all the physical properties of regular Portland cement but are probably as a rule somewhat lower in sand strength than the general run of gray cements.

A number of American Portland cements are quite low in iron and a few are very high. There is a very noticeable difference in the color of these extremes. Color is also due to some extent to the percentage of lime—the higher the lime, the lighter the color.

Of late years numerous authorities have come forward advocating Portland cement containing high percentages of ferric oxide for use in sea water, claiming for such cements great resistance to the disintegrating influence of the salts of magnesium, etc., found in sea water.

A cement, called "Erz Cement," made from a silicious limestone and iron ore is manufactured by the Krupp Steel Co. at Hemmoor, Germany, and is intended for marine construction. It has about the following analysis:

Silica	20.5
Alumina	1.5
Iron oxide	11.0
Lime	63.5
Magnesia	1.5
Sulphur trioxide	1.0

This cement when mixed with plaster and exposed to the action of a concentrated sea water, of five times normal strength, under a pressure of fifteen atmospheres showes no trace of expansion and contraction. Ordinary Portland cement would be destroyed under such conditions in a few days.

Iron cement shows high tensile and compressive strength, provided it is very finely ground, otherwise it is very slow-setting; in fact too slow setting for marine work. American Portland cement containing over 5 per cent iron can be obtained.

Replacing alumina by iron increased the specific gravity of Portland cement.

Magnesia

At one time magnesia was considered dangerous, now the standard specifications allow 5 per cent, and recent investigations place the limit above this. The popular supposition seems to be that magnesia in considerable amounts causes cement in time to expand and crack. Cements in which magnesia replaces lime are of low tensile strength because magnesium compounds have only faint hydraulic properties. A cement made from magnesite and slate had the following analysis:

Silica	27.84
Iron oxide and alumina	11.16
Lime	2.02
Magnesia	56.20
Sulphur trioxide	1.42
Loss	0.86

Briquettes of this cement gave at the end of seven days a neat strength of 31 pounds and at the end of one year a strength of 44 pounds, each figure being the average of five briquettes. Pats made of this cement passed satisfactory boiling and steam tests and the air and cold water pats at the end of two years showed no signs of expansion or cracking. A cement made of dolomite and slate had about 20 per cent the strength of one made of pure limestone and slate, both cements being made to agree with the formula:

$$\frac{\%\ \text{magnesia} \times 1.4 + \%\ \text{lime}}{\%\ \text{silica} + \text{alumina} + \%\ \text{iron oxide}} = 2.$$

Dyckerhoff[1] on the other hand contends that cement containing over 4 per cent magnesia will expand and crack in time and give numerous tests to prove his conclusions and also cites some instances of actual failure of concrete work made with cement

[1] *Tonindustrie-Zeit.*, Feb. 2, 1908, *Cement Age*, Feb., 1909.

high in magnesia. Nearly all experimenters agree that magnesia in cement has practically no hydraulic value.

Bates[1] made a most careful study of the properties of cements containing high percentages of magnesia. His conclusions follow.

Cement can be readily burned in a rotary kiln with a magnesia content of about 9.5 per cent before the resulting clinker will be materially different from that of a cement containing 3 per cent or less. Very high magnesia clinker (over 14 per cent) is very vitreous and dusts slowly, starting within twenty-four hours.

Petrographically no new constituents are present until about 9 per cent MgO is reached when small quantities of "Monticellite," $MgO.CaO.SiO_2$, are noticed; with still increasing amounts spinel, $MgO.Al_2O_3$, occurs. Both of these are non-hydraulic and if the cement is treated with dilute or concentrated hydrochloric acid, are largely insoluble.

Pats made of a cement as high in magnesia as 18.98 per cent were sound after 28 days in air and in water; when placed in boiling water, or steam at the end of twenty-four hours they cracked slightly but were no softer than when removed from the molds. Pats made from cement with lower percentages of magnesia remained in excellent condition after all tests.

Cements containing up to 9.5 per cent magnesia showed normal set with a slight tendency toward slower final set. With a greater content, there was a quick initial set accompanied by a very marked rise of the temperature. With the highest magnesia cement made (19 per cent), the initial set determined with the Vicat needle was quick, accompanied by a rather marked evolution of heat, this heat being rapidly dissipated in the smaller, less insulated pat, gave a slow initial set with the Gilmore needle. The final set was very slow.

The strength developed either by the neat cement or 1 : 3 mortars or 1 : 6 concrete up to periods of half a year, shows that cements containing as much as 7.5 per cent magnesia are satisfactory. Further, the increasing magnesia reduces the rate of hardening, so that at the late periods cements with a higher con-

[1] *Concrete Cement Age*, 1914, p. 29.

tent have rather commendable strengths. Up to this period a 2 per cent solution of equal parts sodium chloride, sodium sulphate, magnesium chloride and magnesium sulphate has no injurious effect.

The question of the economic and satisfactory manufacture of Portland cement from materials high in magnesia is one of great importance in many parts of the world.

Magnesia lowers the clinkering temperature of the cement and hence makes a more fusible clinker, and a more easily burned cement. In view of the evidence recently collected, it seems safe to say that magnesia in cement does not cause unsoundness. At the same time it forms compounds of such weak hydraulic properties that it may be said to constitute an inactive substance and consequently an adulterant in cement.

Whether magnesia should be considered in calculating cement mixtures is a debated point, and one with which the hydraulic value of the magnesian compounds has nothing to do, as the question is simply whether or not the magnesia is combined with silica and alumina in cement. If it does combine, enough of the silica and alumina should be present, not only to form the proper lime compounds, but also the proper magnesia compound, or else the cement will be too basic and will probably contain excess of uncombined lime.

Alkalies

Potash and soda are present in all cements in small quantities, usually less than 0.75 per cent. A large proportion of the alkalies present in the raw material are driven off in burning. Experiments made by the writer with the cement-rock of the Lehigh Valley indicate that at least one-half the potash is lost in the kiln, passing off in the kiln gases. The loss of soda is, of course, much less since this is the less volatile of the two alkalies. It is supposed that the alkalies act as flux and promote the combination of the silica and the alumina with the lime, and experiments made by the writer with small kilns certainly confirm this theory. Several mills have added soda ash in order to make the clinkering of their material more easy. This practice, however, seems to be of doubtful economic advantage.

The addition of small quantities of either the carbonates or the hydroxides of potash and soda will cause cement to set quickly, and it is probable that the presence of any considerable quantity of alkali in cement would cause it to set quickly. When quick-setting cement is due to the presence of the alkalies, the trouble can be remedied, to some extent, by raising the temperature of burning, thus volatilizing the alkali. Cements made from alkali waste often contain large quantities of potash and soda, in some cases the amount reaching as high as 2.5 per cent. Butler[1] states that instances have occurred in which these cements gave anything but satisfactory results, and the only fault that could be found with their chemical composition was a slight excess of alkali. In most cement the alkalies are present in such small quantities that their effects are of little hydraulic importance.

Sulphur

Several compounds of sulphur are present in cement; chief of these are calcium sulphate and calcium sulphide. The action of calcium sulphate upon cement is to delay the set. For this reason it is always added in the form of gypsum or plaster of Paris to the cement after burning. Although the presence of calcium sulphate in small quantities is beneficial to cement, there is no doubt that a quantity exceeding 4 or 5 per cent is injurious.

The standard specifications allow 2 per cent sulphur trioxide (SO_3) in Portland cement. The retrogression sometimes met with in neat Portland cement briquettes is often attributed to the presence of calcium sulphate in the cement. My own experiments, however, made with cements to which no gypsum had been added, and the same cement with the addition of 2 per cent gypsum, do not indicate this, as, in most cases, where retrogression occurred in the cement to which sulphate had been added, it also occurred with the unsulphated cement. Sulphates increase the strength and plasticity of cement, and if they are present in larger amounts than 2 or 3 per cent will often cause higher short time tests than the long period ones, though this may be due merely to the test pieces becoming brittle. The pres-

[1] Portland Cements, by R. D. Butler, p. 263.

ence of sulphates in cement promotes soundness, or at least enables some cements to pass the accelerated tests. The property of gypsum and plaster of Paris to retard the set of cement is touched upon to greater length in the section on "Setting Time."

Carbon Dioxide and Water

Carbon dioxide and water are present in all cements, the amount usually varying with the age of the cement. Freshly-ground cements usually show less than 1 per cent of these two constituents combined, while well-seasoned ones may show as much as 3 or 4 per cent. Underburned cements may, or may not, show high loss on ignition. It is possible to drive off all the carbon dioxide from the raw material, and yet not bring the mass to the point of equilibrium necessary to produce a sound clinker. Samples of underburned clinker will frequently show a loss on ignition (water and carbon dioxide) as low as that of well-burned cement. If the sample is left in the air, however, it soon shows a very high loss on ignition, due to absorption of water and carbon dioxide from the air. Some of the water present in cement can be driven off at 110° C., while some of it requires a red heat for its expulsion. Determinations of loss on ignition, unless very high, are, as a rule, of little help in determining the quality of cement, since an amount as high as 4 per cent may be due to "aging" of the cement, which is recognized as beneficial to it.

It is becoming the practice in the United States to season clinker in the open air in piles. This is done to make the clinker easier to grind. It also allows harder burning because such clinker can be ground as easily after such seasoning as a much softer burned one without it. The effect is also to lower the specific gravity by absorption of water and carbon dioxide.

The attempt was also made to regulate the set of cement by introducing steam into the tube mills and so do away with the addition of gypsum. The attempt does not seem to have been successful, and at any rate the practice has never become general with even the mill which introduced it.

Other Compounds in Portland Cement

Besides the compounds mentioned above, cement usually contains small amounts of titantic acid, Ti_2O_3; ferrous oxide, FeO; manganous oxide, MnO; phosphorus pentoxide, P_2O_5; and strontium oxide, SrO. It is doubtful if these compounds have any effect on the hydraulic or setting properties of Portland cement when present in the minute quantities usually found in commercial cements. It is probable that titanic acid can be substituted for silica, but this cement would be hard to burn; manganese oxide acts as a flux and cements have been made in which strontium replaced lime.

The author found in three Portland cements from the Lehigh District the amounts of the rarer constituents stated below:

	Cement No.		
	1	2	3
Titanic acid	0.28	0.27	0.32
Ferrous oxide	0.23	0.16	0.11
Manganous oxide	0.06	0.08	0.09
Strontium oxide	0.08		
Calcium sulphide	0.18	0.09	0.07
Potash	0.50	0.48	0.59
Soda	0.26	0.31	0.38
Phosphorus pentoxide	0.25	0.31	0.29

MANUFACTURE

CHAPTER III

RAW MATERIALS

Essential Elements

As we have seen from the preceding chapter the essential elements of Portland cement are silica, SiO_2, alumina, Al_2O_3, and lime, CaO. Silica and alumina both exist pure in nature, the first as quartz and flint and the second as corundum or emery. Neither quartz nor corundum are suitable for cement making, because of their extreme hardness and the impossibility of reducing them to the degree of fineness necessary for their combining with the lime. Silica and alumina, however, together are the essentials of clay (or shale) and this is the source of these elements for cement manufacture. Lime is not found free in nature, but combined with carbon dioxide forms calcium carbonate, $CaCO_3$, which occurs in many parts of the country under the names limestone, chalk and marl. Most limestones contain some clay and when this is present to the extent of 18 or more per cent what is known as "cement-rock" or argillaceous limestone results. Certain by-products of other industries contain one or more of the essential elements of Portland cement in a condition, and in proportions suitable for Portland cement manufacture. In this country, blast-furnace slag and caustic soda (alkali) waste are now used.

Classification of Materials

Portland cement may be and is manufactured from a variety of raw materials. Those used may be classed under two general heads, (1) calcareous and (2) argillaceous, according as the lime or the silica and alumina predominate.

Calcareous	Argillaceous
Limestone,	Clay,
Marl,	Shale,
Chalk,	Slate,
Marine shells	Blast-furnace slag.
Alkali waste,	Cement-rock.[1]

Any combination of materials from these two groups may be used which will give a mixture of the proper composition for burning (See Chapter IV), but so far the ones used in this country are:—

1. *Cement-Rock and Limestone.*—Used in the Lehigh Valley cement district of Pennsylvania. This district comprises Berks, Lehigh and Northampton Counties in Pennsylvania, and Warren County, New Jersey.

2. *Limestone and Shale or Clay.*—Used in many parts of the country as these materials are widely distributed.

3. *Marl and Shale or Clay.*—Used principally in Michigan, Ohio and Indiana.

4. *Blast-Furnace Slag and Limestone.*—Plants are now located for the manufacture of cement from these materials in Minnesota, Illinois, Ohio and Pennsylvania.

5. *Caustic-Soda Waste and Clay.*—Used by several plants.

6. *Marine Shells and Clay.*—Used by several plants.

The relative amounts of cement which are made from each class of material are about as follows:

	Per cent
From limestone and clay or shale	62
From cement-rock and limestone	25
From slag and limestone	10
From marl, shells and clay	3

Limestone

Limestone is abundantly distributed throughout the country and occurs in many geological periods. It consists essentially of carbonate of lime (calcium carbonate, $CaCO_3$.) and when pure forms the mineral calcite. The principal foreign elements found in limestone are silica, iron oxide, alumina, carbonate of magnesia and the alkalies, potash and soda. Limestone sometimes

[1] Cement-rock may be considered as either calcareous or argillaceous. Usually it may be classed as the latter, but in the neighborhood of Nazareth, Pa., the rock in several places runs so high in lime as to necessitate the use of slate or clay with it.

contains considerable carbonate of magnesia and when this reaches 45 per cent of the total carbonates it is known as dolomite.

To be suitable for Portland cement manufacture, limestone should contain only a little carbonate of magnesia, 7 per cent being about the limit. Where the limestone is to be used with shale low in magnesia, a little more is allowable, or in other words the amount of carbonate of magnesia in the limestone should not be high enough to cause the magnesia in the finished cement to be more than 5 per cent. This means not above 7 per cent of carbonate of magnesia in the mixture of limestone and shale (or clay).

Where the limestone contains only a few per cent of silica, alumina and iron oxide no attention need be paid to the relative proportions of these latter; but where the limestone contains a considerable portion of these constituents the relation between them should be such that the limestone will when mixed with the shale or clay give a mixture in which the silica and alumina exist in the proper ratio. The amount of ferric oxide in the limestone should not be so high as to cause the amount of ferric oxide in the cement to exceed 4 per cent.

Limestones containing considerable percentages of sulphur, say 5 or 6 per cent, have been successfully employed for cement manufacture. Most of this sulphur is expelled in the kiln. There are a number of limestone deposits through which run small seams of gypsum, notably those of Yankton, S. D. and Portland, Colo. These limestones are used for the manufacture of Portland cement and the product does not contain more sulphur than is allowed by the specifications. The silica combines with the lime, setting free the sulphuric acid, which latter is driven off by the high temperature of the kiln. Limestones should be free from quartz, either in the form of sand or flint pebbles. Occasionally veins of quartz appear in the stone and these may be sorted out in quarrying.

In determining the suitability of a limestone to be used in the manufacture of cement, it is always necessary to take into consideration the shale or clay which is to be used with it, as in

every case it is the mixture of the two, made in proper proportions, which must have the right composition and a shale which contains a low percentage of alumina may very often be used with a limestone containing a high percentage of this latter constituent, etc. By calculating the composition of a proper mixture of the limestone under examination and the shale to be used with it, and then from the calculated analysis of the mixture determining the ratio between the silica and alumina, as well as ascertaining the percentage of magnesia, and iron oxide, the suitability of the limestone and shale may be determined. Directions for making these calculations will be found in the next chapter.

Since the limestone must be reduced to a fine powder in order to intimately mix with the clay or shale used with it, its hardness is to some extent a factor in determining its suitability for cement making, although improved forms of grinding machinery have done much to equalize all classes of material. As a usual thing pure limestone is very much harder than the impure clayey ones, consequently the less pure limestones are really much better for cement manufacture than the hard, pure ones. The greatest factor in the making of a sound cement is the fine grinding of the raw materials. Indeed some plants using limestone and clay have found the grinding of the mixture to the degree of fineness necessary to give the cement a good hot test, when fresh, a very difficult proposition. Some of them have found it preferable on the score of economy not to make their fresh cement pass the soundness test, but to let it season sound in their bins. Such cement provided it *has* seasoned sound is as good as any and there should be no prejudice against its use.

Usually pure limestones require the addition of about one-fifth their weight of dry clay for burning. The approximate proportion in a specific case may be found as follows:

$$\text{Weight of clay} = \frac{(\%\ \text{CaO}) - 42}{42 - (\%\ \text{CaO in clay})} \times 100.$$

The result gives the weight of clay (in pounds) to be added to 100 pounds of limestone. If in the analysis lime is reported as

carbonate of lime, multiply this percentage by 0.56 for the equivalent percentage of lime, CaO, or substitute 75 for 42 in the formula on page 54.

Table XI gives the analyses of some limestones used for Portland cement manufacture together with analyses of the clays or shales employed with them.

Cement-Rock

The impure clayey limestone, used for the manufacture of Portland cement in the Lehigh District, is known techincally as "cement-rock." This rock forms a narrow belt extending in a northeasterly direction from Reading, Pa., to a few miles north of Stewartsville, N. J. It passes through the counties of Berks, Lehigh and Northampton, in Pennsylvania, and Warren County, New Jersey, and is about fifty miles long and not over four miles at its greatest width. There were in May, 1924, located in this district nineteen Portland cement companies in active operation and one in process of construction. The mills of this district produced in 1923 over 25 per cent of the output of the country.

It has been found by experience that a mixture containing about 75 per cent carbonate of lime and 18-20 per cent of clayey matter (silica, iron oxide and alumina) gives the best Portland cement, and the impure limestones found in the Lehigh Valley approach more or less nearly this composition. When this cement-rock contains less than 75 per cent carbonate of lime it is the practice here to add sufficient purer limestones to make the mixture of this proportion. At the mills around Nazareth and at Martins Creek, Pa., the rock contains more than 75 per cent carbonate of lime and here instead of adding limestone it is necessary to add a little clay or cement-rock low in lime to lower the percentage of lime.

Geologically this cement-rock is Trenton limestone of the lower Silurian age, and lies between the Hudson shales and the Kittatinny magnesian limestone. The upper beds of the cement-rock, where it comes in contact with the slate, are more or less shaley in composition and slatey in appearance and fracture. Often here the rock contains less than 50 per cent carbonate of

lime and is not suited for economic reasons to the manufacture of Portland cement. As we go lower in the formation the lime increases until near the base of the formation, in contact with the Kittatinny limestone it may carry as high as 95 per cent carbonate of lime. It is from these lower beds that the limestone necessary for mixing with the cement-rock is obtained. The Kittatinny limestone itself is too high in magnesia (15 to 20 per cent MgO) to use for cement making, but there are a few beds in this formation low enough in magnesia to be used successfully. The cement-rock itself often carries 5 to 6 per cent magnesium carbonate but is never so high in this element as the Kittatinny limestone. The purest limestone in use in the district contains about 98 per cent carbonate of lime and comes from Annville, Pa., some 50-70 miles away.

Cement-rock is considerably softer than the pure limestones, generally used with clay, consequently it is much more easily ground. The nearer it approaches the correct composition for cement mixture the more valuable it is. In general, it may be said that rock requiring a small admixture of clay will prove more economical than one requiring addition of limestone for a proper mixture; since, in nearly every instance, the cement-rock is overlaid by clay which has to be removed anyhow, while the limestone may have to be bought or at least quarried. Equally desirable is the combination of a high and a low cement-rock.

The quantity of limestone added at some of the cement mills in the Lehigh District is as much as 50 per cent of the rock itself, and it is no uncommon thing when limestone is bought to have this item alone cost from 5 to 10 cents per barrel of cement produced. A ton of cement-rock and limestone mixture ready for the kilns will produce from 3.1 to 3.3 barrels of cement. The approximate quantity of limestone necessary to use with any cement-rock whose analysis is known, may be found as follows:—

If the lime is reported as carbonate, $CaCO_3$, quantity limestone necessary.

$$= \frac{75 - (\%\ CaCO_3 \text{ in cement-rock})}{(\%\ CaCO_3 \text{ in limestone}) - 75} \times 100.$$

If the lime is reported as lime, CaO, quantity limestone necessary.

$$= \frac{42 - (\%\ \text{CaO in cement-rock})}{(\%\ \text{CaO in limestone}) - 42} \times 100.$$

The result in either event will be the number of pounds of limestone it is necessary to add to 100 pounds of cement-rock, to make a mixture of approximately correct composition for burning.

In Table XI will be found the analysis of some cement-rocks of the Lehigh District and also of the limestone mixed with them, while Table IX gives a very complete analysis made by the author of a sample of rock of practically exact composition for burning, used by the Dexter Portland Cement Co., Nazareth, Pa. This is followed by an equally complete analysis of a mixture of Annville Limestone and cement-rock, used by the Vulcanite Portland Cement Co., Vulcanite, N. J., made by W. F. Hillebrand, of the U. S. Geological Survey. This mixture is overclayed, however, and undoubtedly is merely a chance sample and not representative of that company's usual practice.

As will be seen by a reference to Table XI, there is considerable difference in the analysis of the various samples. Not only

TABLE IX.—Complete Analyses of Cement-Rock and Cement-Rock Limestone Mixture.

	Cement-rock	Mixture
SiO_2	13.44	15.18
TiO_2	0.23	0.23
Al_2O_3	4.55	4.94
Fe_2O_3	0.56	0.95
Feo	0.88	0.46
FeS_2		0.38
MnO	0.06	0.05
CaO	41.84	40.31
MgO	1.94	1.65
Na_2O	0.31	0.15
K_2O	0.72	0.97
P_2O_5	0.22	0.21
S	0.33	
C	0.75	0.54
CO_2	32.94	32.38
H_2O + 105	155	1.31
H_2O — 105	Dried sample	0.38
	100.32	100.09

is this true between samples from different quarries of the district but also between samples from the same quarry. This latter is shown by Table X, each sample of which represents an average of eleven drill holes of 16 feet each.

TABLE X.—SHOWING THE VARIATIONS IN THE COMPOSITION OF CEMENT-ROCK FROM SAME QUARRY.

Bench	Section of bench	Analysis— SiO_2	$Fe_2O_3+Al_2O_3$	CaO	MgO
First 16 feet	West A	16.26	7.22	70.37	3.95
First 16 feet	West B	14.56	8.64	72.33	3.53
First 16 feet	Center C	16.38	7.90	69.59	3.77
Second 16 feet	West A	17.34	7.94	67.93	4.19
Second 16 feet	West B	18.94	6.98	68.53	3.91
Second 16 feet	Center C	15.54	7.10	71.04	4.12
Second 16 feet	East D	17.02	7.30	69.34	4.16
Second 16 feet	East E	21.36	9.00	65.41	3.96
Third 16 feet	West A	21.98	8.80	62.65	4.87
Third 16 feet	West B	27.00	8.10	69.12	4.73
Third 16 feet	Center C	16.86	8.14	68.54	5.07
Third 16 feet	East D	24.16	9.14	60.69	4.32
Third 16 feet	East E	21.15	9.51	59.09	4.64
Fourth 5 feet	Center C	25.16	8.28	60.42	4.27

Marl

Cement is now made from marl in Michigan, Ohio, New York, and Northern Indiana, and a plant was built (but is now idle) in Virginia to use a shell marl of marine origin.

Marl is more or less pure carbonate of lime, the principle impurities being clay, organic matter and carbonate of magnesia. Marl beds usually occupy the bodies of ancient extinct lakes or else the bottoms and banks of present ones and are formed by the precipitation of calcium carbonate from water by the agency of certain algae or water plants. In many instances the process of making marl beds is still going on. Marl is soft and pulverulent, sometimes containing many small shells, but usually the larger part of it passing a 200-mesh cement testing sieve. It therefore requires little grinding before burning. White marls usually are free from organic matter, but the grey marls often contain from 5 to 10 per cent of impurities. Marl beds vary in size from a few acres up to two or three hundred. Some of the companies in Michigan each had marl beds aggregating over

1,000 acres and measuring an average of 20 feet deep. Prof. Campbell has found that a cubic foot of marl contains 47.5 pounds of marl and generally about 48 pounds of water. As excavated and sent to the mill, however, it frequently contains much more water than the above figure.

Marls for use in Portland cement manufacture should possess the chemical characteristics outlined for limestone and in addition be free from sand and pebbles. It is, of course, possible to separate the former from marl by wash mills and the latter by specially designed screens. Either operation adds to the cost of manufacture, however. Some marls contain a considerable percentage of sulphur. From experiments made by the author, he is inclined to think that most of this sulphur is lost in the kiln. If present in the form of iron pyrites or in combination with organic matter, it is simply burned away. If present as calcium sulphate it is liberated by the combination of the lime with the silica. Exactly how much sulphur is allowable the author is not prepared to say, but it seems probable that at least 5 or 6 per cent SO_3 might be present without rendering the marl unfit for the manufacture of Portland cement. Johnson[1] succeeded in making a sound, true, Portland cement, containing only 1.83 per cent sulphur, in a small experimental kiln from a mixture of clay and gypsum.

Some marls are sticky and pasty in texture and ball together as clay does. Such marls are hard to move from one part of the mill to another and require the addition of more water, which has subsequently to be evaporated in the kilns, in order to pump them about.

The value of a marl bed will usually lie in its depth and area and physical characteristics rather than its chemical composition. Marl must, of course, contain at least 75 per cent of carbonate of lime after drying and deducting the organic matter. What has been said about the chemical requirements of limestone to be used for the manufacture of Portland cement applies equally to marl. The greater the depth of the bed the more economically it can be worked.

[1] *Cement and Engineering News*, January, 1905, p. 11.

Marls usually require the addition of about one-fifth their weight (calculated dry) of dry clay for burning. The approximate amount in any particular case can be found from the formula given on page 54.

Table XI gives the analysis of some marls used for Portland cement making. (Refer to page 68.)

Clay

Clay consists of a mixture of kaolin with more or less sand and other impurities. Kaolin, sometimes called kaolinite, is a hydrated silicate of alumina, having the symbol $Al_2O_3 2SiO_2 2H_2O$. Sand is composed of grains of quartz and other minerals. Clay contains silica both as chemically combined silica in kaolin and the other minerals, and in the free state as quartz sand. Clay also contains more or less iron oxide, lime and magnesia and smaller quantities of potash and soda. Clay originates from the disintegration of rocks containing minerals made up largely of alumina and silica. The most abundantly occurring of these minerals are the feldspars, augite and hornblende. Nephelite and sodalite occur also to a much smaller extent. Decomposition takes place by the gradual leaching out of the more soluble elements of the minerals by water, leaving behind the less soluble ones, silica and alumina, together with smaller proportions of lime, magnesia, iron, potash and soda. These insoluble portions are washed over and over again and deposited in favorable places by water. Such deposits are called sedimentary clay, while clay which, instead of being washed away by water, is left near the rocks from whose decomposition it was formed is called residual clay. The potter deals more particularly with the plasticity, permanence when burnt and refractoriness of clay, but to the Portland cement manufacturer these properties are of very secondary importance. The main thing, of course, is the chemical composition and the state of subdivision in which the silica exists. Roughly speaking, the clay should contain between 2.5 and 4 times as much silica as alumina. There should also not be more iron oxide than alumina in the clay while the best proportion between these two is about 1 to 3. Magnesia and lime are usually present only in small

quantities, the more of the latter present the better, but the former should be low, (not over 3 or 4 per cent). The alkalies should not run over 6 per cent, as an excess is likely to cause unsound and quick-setting cement.

Most clays unless sandy will meet with the above requirements, the usual point to be looked into most carefully is the condition of the silica. All clay contains some uncombined silica, present as quartz sand or pebbles. The latter may be separated from the clay by mechanical means so the former is the one which gives most trouble. The sand must be present in the clay in a very finely divided condition. If much (over 5 per cent) is present in the form of grains not passing a 100-mesh sieve, the clay is unsuited to cement manufacture. Under the section on "Analysis of the Raw Materials" a method is given for determining the quartz sand failing to pass a 100-mesh test sieve. Table XI gives the analyses of clays used in cement manufacture. It should be remembered, however, that in considering the composition of the clay, that of the limestone must also be considered, as the one often supplements the other. What is wanted is a mixture of the two of correct composition and both may be abnormally proportioned and yet give this, the one supplying what the other lacks.

Shale

For practical cement-making purposes shale may be looked upon as merely solidified clay, since the chemical composition of the two are very similar and the same regard must be had as to the state of subdivision of the free silica. Shale is preferable to clay for mixing with limestone since segregation of the two is less likely to take place. It also carries less water and consequently does not require so much drying before grinding. Clays on the other hand are better suited to mixing with marls because of the similarity in physical properties between the two. If a mixture of dry clay and coarsely ground limestone is poured from a spout into a pile the clay will remain in the center of the pile and the limestone will roll down the sides of the pile. Now, if this pile is tapped from below in the middle, as it would be in a bin, the

first material drawn would be most of it clay, while the last of it would be practically all limestone. To overcome this tendency to segregate, therefore, it is best to mix substances of like physical characteristics, shale with limestone and clay with marl.

Table XI gives some analyses of shales used on the manufacture of Portland cement.

TABLE XI.—Analyses of Materials used for the Manufacture of Portland Cement at Various Plants.

Limestone and Clay.

Alpha Portland Cement Co., Catskill Plant, Catskill, N. Y.
(U. S. Geological Survey Bul. No. 243)

	Limestone	Clay
Silica	1.54	61.92
Oxide of iron	1.04	7.84
Alumina	0.39	16.58
Carbonate of lime	96.16	
Lime	53.87	2.01
Carbonate of magnesia	1.09	
Magnesia	0.52	1.58

Ironton Portland Cement Co., Ironton, Ohio.
(Analyses by W. P. Gano)

	Limestone	Shale	Sandstone
Silica	0.92	54.46	84.62
Oxide of iron	3.70	5.66	2.67
Alumina	1.16	23.44	7.22
Carbonate of lime	92.78		
Lime	52.00	0.71	0.61
Carbonate of magnesia	0.97		
Magnesia	0.46	1.00	0.35
Loss on ignition		12.56	

Marquette Cement Manufacturing Co., La Salle, Ill.
(Stuart Smith, Chemist)

	Limestone	Shale
Silica	4.20	59.00
Oxide of iron	0.64	2.66
Alumina	2.11	17.04
Carbonate of lime	90.75	
Lime	50.86	5.51
Carbonate of magnesia	1.84	
Magnesia	0.88	2.80
Sulphuric anhydride	0.17	2.10
Loss on ignition		10.60

TABLE XI.—(*Continued.*)

THE HECLA CO., BAY CITY, MICH.

(Arthur G. Beck, Chemist and Supt.)

	Alpena limestone	Clay
Silica	1.76	46.20
Oxide of iron	0.62	5.57
Alumina	0.62	16.77
Carbonate of lime	96.06	
Lime	53.83	8.62
Carbonate of magnesia	1.51	
Magnesia	0.72	5.22
Sulphuric anhydride		0.68
Loss on ignition		13.34

SECURITY CEMENT AND LIME CO., SECURITY, MD.

(From Maryland Geological Survey, Vol. VIII)

	Limestone	Shale
Silica	6.04	62.60
Oxide of iron	0.62	5.23
Alumina	1.96	21.25
Carbonate of lime	87.25	
Lime	48.88	0.36
Carbonate of magnesia	3.64	
Magnesia	1.74	0.94
Loss on ignition	39.30	

TIDEWATER PORTLAND CEMENT CO., UNION BRIDGE, MD.

(Analyses by author)

	Pure limestone	High silica limestone	Shale
Silica	0.28	6.40	54.54
Oxide of iron	0.24	0.62	9.80
Alumina	0.24	0.62	24.24
Carbonate of lime	97.23	91.14	
Lime	54.49		0.85
Carbonate of magnesia	2.83	1.38	
Magnesia	1.35		1.78

ALABAMA PORTLAND CEMENT CO., DEMOPOLIS, ALA.

(Analysis reported by T. G. Cairns, Gen. Mgr.)

	Chalk
Silica	9.88
Oxide of iron	6.20
Alumina	6.20
Carbonate of lime	77.12
Lime	43.22
Carbonate of magnesia	1.08
Magnesia	0.52
Loss on ignition	5.72

TABLE XI.—(*Continued.*)

ATLANTIC AND GULF PORTLAND CEMENT CO., RAGLAND, ALA.
(C. N. Wiley, Chemist)

	Limestone	Shale
Silica	1.80	63.90
Oxide of iron	0.46	7.68
Alumina	0.74	21.07
Carbonate of lime	94.66	
Lime	53.03	trace
Carbonate of magnesia	2.24	
Magnesia	1.07	1.52
Sulphuric anhydride	none	none
Loss on ignition	42.95	4.91

STANDARD PORTLAND CEMENT CO., LEEDS, ALA.
(C. M. Goodman, Chemist and Supt.)

	Limestone	Shale	Sandstone
Silica	2.10	57.11	92.48
Oxide of iron	0.82	7.91	1.69
Alumina	0.82	20.76	2.69
Carbonate of lime	94.32		
Lime	52.84	2.27	1.50
Carbonate of magnesia	2.92		
Magnesia	1.40	7.90	0.83
Sulphuric anhydride			
Loss on ignition	42.90	2.16	

TEXAS PORTLAND CEMENT CO., TEXAS.
(H. R. Durbin, Chemist)

	Limestone	Shale
Silica	6.07	55.40
Oxide of iron	2.20	5.45
Alumina	3.76	22.54
Carbonate of lime	85.48	
Lime	47.89	3.19
Carbonate of magnesia	1.17	
Magnesia	0.56	0.25
Sulphuric anhydride	0.30	1.32
Sulphur		0.48
Loss on ignition	39.20	9.88

ST. LOUIS PORTLAND CEMENT WORKS, ST. LOUIS, MO.
(John Taylor, Manager and Chemist)

	Limestone	Shale
Silica	1.00	56.60
Oxide of iron	0.35	6.00
Alumina	0.65	20.70
Carbonate of lime	95.00	
Lime	53.24	1.00
Carbonate of magnesia	2.00	
Magnesia	0.96	1.75
Sulphuric anhydride		0.75
Loss on ignition		11.20

TABLE XI.—(*Continued.*)

IOLA PORTLAND CEMENT CO., IOLA, KANS.
(Analyses reported by H. Struckmann, Genl. Mgr.)

	Limestone	Shale
Silica	1.16	54.36
Oxide of iron	1.72	7.75
Alumina	0.58	18.57
Carbonate of lime	92.59	
Lime	51.87	7.44
Carbonate of magnesia	3.36	2.40
Sulphuric anhydride		
Loss on ignition	43.28	9.76

UNITED KANSAS PORTLAND CEMENT CO., IOLA, KANS.
(E. C. Champion, Chemist and Supt.)

	Iola limestone	Concrete shale
Silica	2.00	38.62
Oxide of iron	0.92	5.46
Alumina	0.52	19.20
Carbonate of lime	93.04	5.77
Lime	52.14	
Carbonate of magnesia	3.25	
Magnesia	1.55	1.90
Sulphuric anhydride		0.15
Loss on ignition		8.90

OKLAHOMA PORTLAND CEMENT CO.
(W. S. Creveling, Chemist)

	Limestone	Shale
Silica	0.42	42.30
Oxide of iron	0.10	5.92
Alumina	0.71	12.36
Carbonate of lime	98.32	
Lime	55.08	12.86
Carbonate of magnesia	0.59	
Magnesia	0.28	5.50
Lead oxide	0.32	
Loss on ignition	43.11	18.11

THE NORTHWESTERN STATES PORTLAND CEMENT CO., MASON CITY, IO.
(Geo. P. Diekmann, Chemist)

	Limestone	Clay
Silica	1.20	55.60
Oxide of iron	0.32	5.24
Alumina	0.56	16.39
Carbonate of lime	96.50	
Lime	54.08	6.29
Carbonate of magnesia	1.10	3.04
Sulphuric anhydride		1.14
Loss on ignition		11.60

THREE FORKS PORTLAND CEMENT CO., TRIDENT, MONT.
(R. E. Edelhoff, Analyst)

	Limestone	Cement-rock
Silica	8.00	16.54
Oxide of iron	1.16	1.31
Alumina	3.30	5.37
Carbonate of lime	83.83	72.42
Lime	46.98	40.59
Carbonate of magnesia	2.87	3.04
Magnesia	1.38	1.46
Loss on ignition	38.69	33.42

HENRY COWELL LIME & CEMENT CO., COWELL, CAL.
(C. E. Kline, Chemist)

	Limestone	Clay
Silica	0.66	55.12
Oxide of iron	0.26	6.20
Alumina	1.40	20.00
Carbonate of lime	95.40	
Lime	53.47	3.26
Carbonate of magnesia	1.51	
Magnesia	0.72	1.73
Sulphuric anhydride		1.64
Loss on ignition		10.70

PACIFIC PORTLAND CEMENT CO., SUISUN, CAL.
(U. S. Geological Survey, Bul. No. 243)

	Travertine limestone	Clay
Silica	1.21	58.25
Oxide of iron	0.50	7.35
Alumina	0.70	18.56
Carbonate of lime	95.62	
Lime	53.62	3.10
Carbonate of magnesia	0.92	
Magnesia	0.44	1.28
Sulphuric anhydride	0.11	0.45
Loss on ignition	42.98	8.55

SANTA CRUZ PORTLAND CEMENT CO., DAVENPORT, CAL.
(Llewellyn T. Bachman, Chemist)

	Limestone	Clay	Shale
Silica	2.03	55.04	65.25
Oxide of iron	0.31	6.12	2.56
Alumina	1.37	20.72	6.95
Carbonate of lime	94.69		
Lime	53.06	3.08	3.86
Carbonate of magnesia	1.96		
Magnesia	0.95	2.17	0.98
Sulphuric anhydride		1.76	1.30
Loss on ignition	41.96	8.64	19.17

TABLE XI.—(*Continued.*)

SUPERIOR PORTLAND CEMENT CO., CONCRETE, WASH.
(Chas. A. Newhall, Chemical Engineer)

	High grade limestone	Low grade limestone	Shale
Silica	5.08	11.63	57.36
Oxide of iron	2.28	2.01	8.00
Alumina	2.28	2.01	16.78
Carbonate of lime	92.50	85.69	
Lime	51.84		5.35
Carbonate of magnesia	0.12	0.66	
Magnesia	0.06		4.11
Sulphuric anhydride			trace
Loss on ignition			5.34

Cement-Rock and Limestone.

ALLENTOWN PORTLAND CEMENT CO., EVANSVILLE, PA.
(Made by the author)

	Cement-rock	Local limestone	Annville limestone
Silica	15.06	2.79	0.36
Oxide of iron	1.30	0.68	0.45
Alumina	3.60	0.68	0.45
Carbonate of lime	73.64	94.63	97.11
Lime	41.27		
Carbonate of magnesia	3.34	1.80	1.12
Magnesia	1.60		

DEXTER PORTLAND CEMENT CO., NAZARETH, PA.
(Made by the author)

	High lime cement-rock	Low lime cement-rock
Silica	11.10	18.15
Oxide of iron	1.24	1.61
Alumina	4.42	7.21
Carbonate of lime	77.60	68.14
Lime	43.49	
Carbonate of magnesia	4.17	3.88
Magnesia	1.99	1.86

EDISON PORTLAND CEMENT CO., STEWARTSVILLE, N. J.
(Made by the author)

	Cement-rock	New Jersey calcite
Silica	16.16	0.46
Oxide of iron	1.25	0.36
Alumina	6.98	0.36
Carbonate of lime	70.38	96.60
Lime	39.44	54.14
Carbonate of magnesia	3.90	3.54
Magnesia	1.82	1.66

TABLE XI.—(*Continued.*)

NORTHAMPTON PORTLAND CEMENT CO., STOCKERTOWN, PA.
(Made by the author)

	Cement-rock	Local limestone
Silica	18.94	3.66
Oxide of iron	1.56	2.10
Alumina	5.42	2.10
Carbonate of lime	68.53	92.13
Lime	38.41	
Carbonate of magnesia	3.91	2.21
Magnesia	1.87	1.06

Marl and Clay.

MICHIGAN PORTLAND CEMENT CO., COLDWATER, MICH.
(Analyses by H. E. Brown)

	Marl		Cold Water Shale
Silica	0.15	8.60	57.26 to 61.25
Oxide of iron	0.19	1.54	6.53 " 8.30
Alumina	0.27	1.30	18.12 " 21.59
Carbonate of lime	54.69	82.51	
Lime	97.52	46.20	1.25 " 1.50
Carbonate of magnesia	1.85	5.84	1.49 " 2.31
Magnesia	0.88	2.78	
Sulphuric anhydride			0.65 " 1.34
Organic matter	0.05	10.50	
Loss on ignition			6.19 " 8.32

WABASH PORTLAND CEMENT CO., STROH, IND.
(U. S. Geological Survey, Bul. No. 243)

	Marl	Clay
Silica	0.66	57.74
Oxide of iron	0.62	17.76
Alumina	0.62	17.76
Carbonate of lime	94.91	
Lime	53.17	7.80
Carbonate of magnesia	0.98	
Magnesia	0.47	3.52
Sulphuric anhydride		
Loss on ignition	42.35	12.30

Blast-Furnace Slag

In 1897 the Clinton Cement Co. in connection with the Clinton Iron and Steel Co., erected a small plant for the manufacture of Portland cement from limestone and slag, at Pittsburgh, and in 1900, the Illinois Steel Co. began the manufacture of Portland cement from blast-furnace slag and limestone at their South Chi-

cago works. This company later became the Universal Portland Cement Co., with works at Buffington, Ind., Universal, Pa., and Deluth, Minn.

There are two kinds of cement made from blast-furnace slag and the two must not be confused, one a *true Portland* made by mixing limestone and slag, grinding very finely the resulting mixture and then *burning,* just as if the raw materials were clay and limestone or cement-rock and limestone; the other a puzzolan or slag cement made by grinding with slaked lime suitable slag, which has been previously chilled suddenly by dropping into water. The resulting mixture is then ready for use and is not burned.

At the plants of the Universal Portland Cement Co. the slag is granulated by cooling it suddenly with water, dried, ground, and then mixed with the proper proportion of ground limestone.

Slag suitable for the manufacture of Portland cement can only come from furnaces working on pure ores, such as those of the Lake Superior mines, and fluxed with low magnesian limestone. Generally speaking, the slag must analyze within the following limits:

Silica, plus alumina, not over 48 per cent.

Iron and alumina, 12 to 14 per cent.

Magnesia, under 3 per cent.

There is a slight thermal advantage in using slag for the manufacture of Portland cement. The lime is present as oxide, just as it is in cement, and no heat is required to decompose, as is the case with limestone where heat is required to change the carbonate to oxide.

This advantage, however, is negatived to some extent by the necessity of driving off the water used to granulate the slag. Even were this latter not the case, under the present wasteful system of burning cement, this saving would hardly be appreciable.

Below is an analysis of a typical slag used by the Universal Portland Cement Co. in making their "Universal" Portland cement.

	Per cent
Silica	33.10
Iron oxide and alumina	12.60
Lime	49.98
Magnesia	2.45

Concrete Cement Age gives the following as the analysis of materials used in the new Ford cement plant at Detroit, Mich.

	Slag	Limestone
Silica	30—40%	1.75 max.
Alumina	10—17%	1.75 "
Magnesia	5% max.	1.00 "
Lime	Balance	96.00 min.

Alkali Waste

The precipitated calcium carbonate obtained from the manufacture of caustic soda by the Leblanc process has been used successfully in Europe for the manufacture of Portland cement. The Michigan Alkali Co., Wyandotte, Mich., in 1899, built a small plant designed to take care of 100 tons of waste. This plant is now operated by the Wyandotte Portland Cement Co. It seems hardly likely that alkali waste will be used to any extent in this country in view of the availability of much more suitable materials and the fact that the material is now being reburned to lime by those who formerly discarded it. Those who are interested in the process, however, will find a paper of some length on the subject in *Cement and Engineering News* of March and April, 1900.

Below is an analysis of the alkali waste used by the Michigan Alkali Co.

	Per Cent
Silica	0.60
Alumina and iron oxide	3.04
Carbonate of lime	95.24
Carbonate of magnesia	1.00
Alkalies	0.20

Gypsum

Gypsum either in its native state or after calcining is always added to Portland cement to regulate the set for reasons which will be explained in Chapter XXI, and hence may be considered as one of the raw materials of its manufacture. Gypsum consists of hydrated sulphate of lime, $CaSO_4.2H_2O$. This is usually contaminated by the presence of more or less silica, iron

and alumina, carbonates of lime and magnesia, organic matter and sulphides. Gypsum is found in many localities in this country and in Nova Scotia and New Brunswick.

When gypsum is heated to 132° C. it loses three-fourths of its water of crystallization and another hydrate is formed having the formula $(CaSO_4)_2.H_2O$ and commonly known as plaster of Paris or calcined plaster. If gypsum is heated to a temperature of 343° C. all the water is driven off and it is converted to anhydrite which has the formula $CaSO_4$, and is known usually as dead burned plaster.

Either gypsum or plaster of Paris may be used to slow the set of cement. If the retarder is to be added to the clinker before the latter is ground, gypsum is generally used. If the addition is to be made at the stock house, when the cement is being packed, finely ground plaster of Paris is used. In valuing gypsum or plaster of Paris for cement manufacture, the main requisite is the quantity of sulphate of calcium or SO_3 it contains, and the purchaser has to take into consideration chiefly how much of this he is getting for his money. In the case of plaster of Paris its fineness should also be taken account of, if it is to be added to ground cement. The finer the plaster, the better it is for this purpose.

A cement mill manufacturing 1,000 barrels a day will use about 4 tons of gypsum or plaster per day. This is usually purchased from some dealer and arrives at the mill either in bags or in bulk the gypsum being crushed to pass an inch perforated screen.

Below are the analyses of some gypsums used in retarding the set of Portland cement:

TABLE XII.—SHOWING ANALYSIS OF SOME GYPSUMS USED IN THE MANUFACTURE OF PORTLAND CEMENT.

From	SiO_2	$Al_2O_3+Fe_2O_3$	$CaCO_3$	$MgCO_3$	$CaSO_4$	H_2O
Nova Scotia....	0.10	0.04	0.56	0.11	78.51	20.90
Michigan	1.31	0.64	0.27	0.18	76.83	20.01
Kansas	1.18	0.15	0.36	0.52	78.04	19.98
New York	2.11	0.61	1.18	0.65	76.51	19.36
Ohio	0.68	0.16	/		78.08	28.14

The Valuation of Raw Materials

In passing on the availability of raw material for cement manufacture, a number of things must be considered besides mere analysis. The cost of quarrying or excavating, the power required to grind and the coal it will take to burn it must be considered. With excavating we include also cost of conveying to the mill. Marl and clay are the easiest raw materials to excavate, but on the other hand the mill can seldom be located near the beds of the former, owing to the necessity of having the mill located on firm dry ground. This necessitates pumping or carrying the marl, in some instances several miles, and increases the cost of manufacture. A very shallow marl bed can not be worked as economically as a deep one because of the constant moving about of the excavating apparatus, etc. When marl beds are located in the north, cold weather is apt to tie them up by freezing of the lake over them, necessitating either the cutting of the ice or the shutting down of the mill. Both add to the cost of production.

Cement-rock is usually blasted down, loaded on cars and hauled by cable to the mill, close at hand. It costs more in powder and drilling than marl, but, if a steam shovel is used to load the cars, costs less after it is down to convey to the mill than marl, as only half as much material has to be handled owing to the water in the marl. Even when loaded by hand the cost of quarrying cement-rock is no greater than for marl.

Limestone is harder than cement-rock and costs more to drill, blast and break up the lumps into sizes suitable for loading on the cars or carts. Shale will cost about the same as cement-rock to quarry and load, but the mill is usually located near the limestone deposit or marl beds, as much more of these are needed, consequently the shale must usually be carried some distance to the mill. The cost of getting out either cement-rock or limestone will be influenced by the amount of "stripping" that has to be done. In some mills this top can be used, in which case this cost is saved.

Marl and clay are the easiest materials to grind, shale, cement-rock and chalky limestone come next, while limestone and slag

are harder still. Slag is brittle but hard, breaks up to a size passing a 20-mesh sieve easily, but requires considerable additional grinding to make 95 per cent of it pass a 100-mesh sieve.

As a general rule cement-rock-limestone mixtures burn easiest of any of the combinations in the kilns, limestone-clay and slag-limestone mixtures are harder still and the wet marl and clay mixture requires much more coal than any other. In this case, burning and drying are considered together. Cement-rock seldom contains more than 5 per cent moisture and limestone even less as they come from the quarry. Slag may carry 15 or 20 per cent of water left in from the process of granulation, and marl 50 to 60 per cent. The more intimate mixture of the argillaceous and calcareous elements of the cement-rock limestone mixture makes it easier to burn than an equally dry limestone-clay combination, while the large quantity of water to be driven off in the kilns makes the burning of the marl-clay combination so costly. If marl and clay are introduced into the kiln dry they require no more fuel to burn than the cement-rock-limestone combination. The subjects of burning and grinding are treated of to greater length in special chapters and these should be consulted for data relative to the cost of manufacturing Portland cement from various kinds of raw material.

Portland cement can be made from such a variety of materials that almost every geological report will show analyses of hundreds of limestones, clays, shales and marls suitable for the manufacture of cement.

The mere fact therefore that raw materials of suitable chemical composition for the manufacture of Portland cement exists in a certain locality is no occasion for the erection of a mill on this site, because the success of the enterprise will depend more upon local conditions than upon the raw materials themselves.

The cost of fuel, labor and supplies must be taken into consideration as well as the ability to market the product. The fuel item in the manufacture of Portland cement is a big one, dry material requiring from 100 to 200 pounds, under the usual system, for burning and grinding.

Portland cement is so bulky in proportion to its value that the nearness of the mill to market is one of the most important items.

The Lehigh District is blessed with a soft, easily-ground cement-rock, but it probably owes its development also to cheap coal and labor, experienced men and its proximity to such markets as New York, Philadelphia and Boston.

CHAPTER IV

PROPORTIONING THE RAW MATERIALS

While a glance at the table of analysis on page 19 will show wide variation in the chemical composition of Portland cement, it must not be supposed that such latitude in proportioning the raw materials really exists. If the resulting Portland cement is to be sound, normal setting, and of good strength, it is imperative that the raw materials shall be correctly proportioned, as to the balance between the silica and alumina on the one hand and the lime on the other. Cements from different mills often vary several per cent from each other as to the silica, lime and alumina, and yet one appears as good as the other. This variation in composition is due in part to addition of gypsum to, and the contamination by the coal ash of the clinker and also to the absorption of carbon dioxide from the air. It is still, however, evident that this will not account for all the variations, and that the raw mixtures from which cement is made vary widely, within certain limits, at the different works.

Many attempts have been made to put the calculation of cement mixtures on a strictly scientific basis and numerous "formulas" have been proposed for expressing the relation between the lime on the one hand and the silica, iron oxide and alumina on the other. Michaelis, Le Chatelier and Newberry all derived such formulas from the result of their experiments on the composition of cement.

Lime Ratio

Michaelis[1] based his formula on the hydraulic index, and indeed it may be considered as the reciprocal of this, or the ratio between the percentage of lime and the combined percentages of silica, alumina and iron oxide present in Portland cement. He states that this ratio must lie within the limits of 1 to 1.8 and 1 to 2.2, and practically all American cements satisfy this formula. He proposes the empirical figure 2. His formula stated in the form of an equation is:

[1] *Cement and Engineering News*, August, 1900.

$$\frac{\%\ \text{lime}}{\%\ \text{silica} + \%\ \text{iron oxide} + \%\ \text{alumina}} = 2.$$

The writer has found that while this formula will in some instances give a mixture which would result, when burned, in a very much overclayed, underlimed and consequently quick-setting cement, still taken as a whole it is as satisfactory as any of the formulas based on molecular weights. The fixed ratio of 2 does not seem to be applicable to all cases, though this is probably often due as much to manufacturing conditions as to composition of the material. Of four cements analyzed by the writer, each from a different mill, the ratios were: A 1.92, B 2.01, C 2.07, D 2.18. Any cement made at mill D with this formula would have been decidedly quick-setting. When the contamination of the cement by the fuel ash is taken into consideration it is probable that A is the only one of these four cements in which the ratio between the lime and the silicates before burning was as low as 2.

The writer has found that in his experimental work, where the raw materials were ground to a fineness of 95 per cent through a No. 100 test sieve, it has always been possible to make a sound cement, of normal setting properties and good strength when the composition of this cement met the ratio:

$$\frac{\%\ \text{lime}}{\%\ \text{silica} - \%\ \text{iron oxide} - \%\ \text{alumina}} = 2.05.$$

provided the ratio between the silica and the alumina was not less than 2.5 to 1 nor more than 5 to 1.

In mill practice, however, it is seldom that as high a ratio as this can be carried. Just what the ratio should be depends upon conditions of manufacture and the nature of the materials. When the alumina is low, this ratio is often carried as low as 1.9 without obtaining quick-setting cement. On the other hand, when the alumina is high, it is often, but not always, necessary to carry the ratio as high as 2.05 to avoid quick-setting cement.

The formula used to proportion the raw materials so as to give a cement having a definite ratio between the lime and the silica, alumina and iron oxide is as follows.

$$\frac{\text{Limestone (or marl)}}{\text{Clay (or shale or cement-rock)}} = \frac{(\%\ SiO_2 + \%\ Fe_2O_3 + \%\ Al_2O_3 \text{ in clay}) \times R - (\%\ CaO \text{ in clay})}{(CaO \text{ in limestone}) - (\%\ SiO_2 + \%\ Fe_2O_3 + \%\ Al_2O_3 \text{ in limestone} \times R)}$$

Where coal is used as a fuel and a ratio of 2.05 is desired R should be about 2¼.

The additional 0.2 added in the formula is to take care of the small amount of coal ash which enters the cement.

If in the analysis, the lime is given as carbonate of lime, 2¼ becomes 4, for CaO : CaCO :: 56 : 100 :: 2¼ : 4.

Where a lower ratio is desired R is reduced accordingly.

As an example of the use of the formula suppose we wish to calculate the proper mixture of cement-rock and limestone of the following analyses.

ANALYSES.

	Cement-rock	Limestone
Silica	19.06	2.14
Iron oxide	1.14	0.46
Alumina	4.44	1.00
Carbonate of lime	69.24	94.35
Carbonate of magnesia	4.21	2.18

The calculation is as follows:

$$\frac{\text{Limestone}}{\text{Cement-rock}} \quad \frac{(19.06 + 1.14 + 4.44) \times 4 - 69.24}{94.35 - (2.14 + 0.46 + 1.00) \times 4} = \frac{29.32}{79.95}$$

Or for 100 part cement-rock there will be required.

$$\frac{29.32 \times 100}{79.95} = 36.7 \text{ parts limestone.}$$

Newberry's Formula

Newberry followed up his paper on the constitution of Portland cement, mentioned in Chapter II, with the first formula, based on scientific rather than empirical knowledge, of which the writer knows. Considering cement to be composed of tricalcium silicate, $3CaO.SiO_2$, containing 2.8 times as much lime

as silica, and dicalcium aluminate, $2CaO.Al_2O_3$, containing 1.1 times as much lime as alumina, he proposed the following:

Lime = silica × 2.8 + alumina × 1.1.
Carbonate of lime = silica × 5 + alumina × 2.

As this formula represents the maximum of lime which a cement could carry, if it were manufactured under ideal conditions as to grinding and burning, conditions which are never met with in practice, he found it necessary in actual work to carry the lime a little lower than called for by the formula, say between 95 and 98 per cent of the maximum. Ninety-five per cent of the maximum would give the following:

Carbonate of lime = silica × 4.8 + alumina × 1.9.

Newberry's formula would make a cement containing 23 per cent silica and 6 per cent alumina contain $(23 \times 2.8 + 6 \times 1.1) \times 0.9 = 63.9$ and one containing 21 per cent silica and 8 per cent alumina contain $(21 \times 2.8 + 8 \times 1.1) \times 0.9 = 60.8$. As a matter of fact there is no such difference between high silica and high alumina cements, as Table VIII will show.

Later researches have shown Newberry was in error in considering alumina as present in the form of a dicalcium aluminate and all the silica as tricalcium silicate. His formula is therefore now obsolete so far as being a scientific expression of the composition of cement goes, although it may have empirical value.

Formula Based on Bates and Rankin's Work

The author suggests the following method of arriving at a scientific formula for expressing the correct relation between the various elements in cement.

Referring to Chapter II it will be recalled that Rankin found the essential compounds in cement to be the dicalcium silicate, the tricalcium silicate and the tricalcium aluminate. Bates considers that the two silicates should be present in about equal proportions. These chemists also concluded that magnesia re-

places lime and iron oxide combines as alumina. The relation between these various compounds is then:

Silica $\times$ 3.8 = lime combined as tricalcium silicate.
Silica $\times$ 1.9 = lime combined as dicalcium silicate.
Alumina $\times$ 1.7 = alumina combined as tricalcium aluminate.
Iron oxide $\times$ 0.6 equivalent to alumina.
Magnesia $\times$ 1.4 equivalent to lime.
Sulphur trioxide $\times$ 0.7 equivalent to lime.

If the two silicates are to be present in about equal proportions the formula for a three-component cement would then be:

$$\text{Silica} \times 2.3 + \text{alumina} \times 1.7 = \text{lime}.$$

Or taking the iron oxide, magnesia and sulphur trioxide into consideration:

$$\text{Silica} \times 2.3 + (\text{alumina} + \text{iron oxide} \times 0.6) \times 1.7 = \text{lime} + \text{magnesia} \times 1.4 - \text{sulphur trioxide} \times 0.7.$$

This formula may be somewhat simplified as follows:

$$\text{Silica} \times 2.3 + \text{alumina} \times 1.7 + \text{iron oxide} = \text{lime} + \text{magnesia} \times 1.4 - \text{sulphur trioxide} \times 0.7.$$

The analyses below give examples of cements which satisfy this formula.

	A Per cent	B Per cent	C Per cent
Silica	22.0	19.4	23.0
Alumina	7.5	9.2	5.4
Iron oxide	2.5	4.1	3.1
Lime	62.6	63.1	63.8
Magnesia	2.5	1.6	1.7
Sulphur trioxide	1.5	1.2	1.5
Loss on ignition, etc.	1.5	1.4	1.5

Use of above Formula

This formula may be used for proportioning the raw materials. The method of doing this can be best explained by an example.

Let us suppose we wish to make a mix of clay and limestone of the following composition:

		Clay Per cent	Limestone Per cent
Silica		63.0	2.0
Alumina		20.0	0.8
Iron oxide		7.0	0.5
Lime		1.0	53.0
Magnesia		1.0	1.0
Loss on ignition, etc.		8.0	42.7
	Limestone.		
Lime		53.0	
Magnesia	$1 \times 1.4 =$	1.4	54.4
Silica	$2 \times 2.3 =$	4.6	
Alumina	$0.8 \times 1.7 =$	1.4	
Iron oxide		0.5	6.5
Available lime			47.9
	Clay.		
Silica	$63 \times 2.3 =$	144.9	
Alumina	$20 \times 1.7 =$	34.0	
Iron oxide		7.0	185.9
Lime		1.0	
Magnesia	$1 \times 1.4 =$	1.4	2.4
Required lime for 100 parts			183.5

The number of parts of limestone required for 100 parts of clay will then be

$$\frac{183.5 \times 100}{47.9} = 383.$$

Or the mix should consist of

	Per cent
Clay	21
Limestone	79

If burned with oil, this will give a cement in which the relation between the lime and silica and alumina will be satisfactory. If burned with coal, the ash of the latter will disturb the balance and make the cement overclayed. Allowance should therefore be made for the ash. The simplest method will be to consider the ash as clay and reduce the latter in the mix to correspond with the percentage of ash in the fuel, etc.

For example: Six hundred pounds of mix will consist of 126 pounds of clay and 474 pounds of limestone. About one-half the coal ash enters the clinker. If the coal has 12 per cent ash and one hundred pounds of coal are required to burn a barrel of cement, then 6 pounds of ash enter the clinker and deducting this amount of clay our percentages would be:

	Per cent
Clay	20
Limestone	80

The above formula will be found of service in proportioning materials with which the chemist has had no experience, but for everyday mill control work the formula given on page 77 will be found in most instances just as satisfactory and much simpler.

Fixed Lime Standard

While the above formulas are employed very frequently for calculating cement mixtures from complete analysis, as in making laboratory trial burnings, or when starting a new mill, or opening a new deposit, it will be found more practicable in actual mill routine work, to fix upon a certain percentage of carbonate of lime found to give satisfactory results by experience and to keep the mixture as near this as possible.

Provided the amount of water, organic matter and magnesia is constant in the raw materials, it will be comparatively easy to keep a pretty uniform mixture by merely watching the percentage of carbonate of lime. In the cement-rock-limestone mixtures of the Lehigh District the conditions are very constant and it is the usual practice here to "control the mix" by keeping the percentage of carbonate of lime in it around a fixed point (usually 74.5 to 75.5), the standard varying at different mills. In most mills using limestone-clay mixtures, very much the same conditions obtain, the magnesia and water remaining fairly constant and organic matter being present only in very small percentages.

Some clays show considerable variations in different parts of the bed in the relative proportions of the silica and the alumina to each other. In this event, the clay should be so worked as

to give a constant ratio between the silica and the alumina. By doing this a constant lime standard may be held to and a cement of more uniform setting properties will result. In the marl-clay mixtures water and organic matter are apt to vary widely and in order to make a uniform mix it is necessary to do more than merely determine the lime in the slurry, as the wet mixture of marl and clay is called. When the organic matter is constant it is merely necessary to dry the mixture and determine the carbonate of lime as in a limestone-cement-rock or limestone-clay mixture.

In controlling the mixture by a carbonate of lime determination it is necessary that the ratio between the silica and alumina be kept constant, this can usually be done without difficulty after a thorough prospecting of the raw materials. This problem will usually be simplified by having the quarrying operations spread out over the whole face, and on several ledges, and not confined to one particular spot. For instance, suppose a quarry to have a face of 500 feet and a depth of 48 feet and to be worked in benches of 16 feet each. It will be a simpler matter to keep a constant ratio between the silica and the alumina by distributing the shovels at different locations and blasting down the entire face by means of well drills, than it would be by localizing the work at one point.

Formulas for a Fixed Lime Standard

The mathematical part of calculating cement mixtures for a fixed lime standard may be simplified by the following formulas, which have been used by the writer in his work.

The first formula is for use when the cement-rock is weighed and the proper proportion of this weight of limestone is added.

1. To find the percentage of a given limestone to be added to a given cement-rock or clay to make a given mixture.

Let—

X = Percentage of limestone necessary.
L = Percentage of $CaCO_3$ in limestone.
R = Percentage $CaCO_3$ in the rock or clay.
M = Percentage of $CaCO_3$ desired in the mixture.

Then—

$$X = \frac{M - R}{L - M} \times 100.$$

Example—What percentage of limestone analyzing 95 per cent $CaCO_3$ must be added to a cement-rock analyzing 70 per cent $CaCO_3$ to give a mix analyzing 75 per cent $CaCO_3$?

$$\text{Percentage of limestone} = \frac{75 - 70}{95 - 75} \times 100 = \frac{500}{20} = 25.$$

Hence to every 100 pounds of cement-rock 25 pounds of limestone must be added.

The next formula is practically the same as the last only it is intended for use when the limestone or marl is weighed and the proper proportion of this weight of clay or shale is added.

2. To find the percentage of a given clay or shale (or cement-rock) to be added to a given marl or limestone to make a given mixture.

Let—

X = Percentage of clay or shale necessary.
C = Percentage of CaO in clay or shale.
L = Percentage of CaO in marl or limestone.
M = Percentage of CaO desired in the mixture.

Then—

$$X = \frac{L - M}{M - C} \times 100.$$

Example—What percentage of clay analyzing 2.5 per cent CaO must be added to a limestone containing 53 per cent CaO to obtain a mixture analyzing 41 per cent CaO?

$$\text{Percentage clay} = \frac{53 - 41}{41 - 2.5} \times 100 = \frac{1.200}{38.5} = 31.$$

Instead of percentages of CaO percentages $CaCO_3$ may be used, but if used in one case, it must be used in all.

It sometimes happens that it is more convenient to divide the mix into percentages of limestone and of cement-rock or clay than to make one constituent a certain percentage of the other. For

example, when both the limestone and cement-rock are already in storage and both are weighed into the same hopper, it makes fewer dumps necessary, to fill the hopper full each time and to so proportion the limestone and clay as to just do this. The following formula will give the percentage of both the calcareous and argillaceous constituents of the mixture.

3. To find the percentage of a given cement-rock and of a given limestone for a given mix.

Let—

X = Percentage of cement-rock, shale or clay.
Y = Percentage of limestone or marl.
R = Percentage of $CaCO_3$ in cement-rock, shale or clay.
L = Percentage of $CaCO_3$ in limestone or marl.
M = Percentage of $CaCO_3$ desired in the mixture.

Then—

$$Y = \frac{M - R}{L - M} \times 100.$$

$$X = 100 - Y.$$

Example—What percentage of limestone analyzing 95 per cent $CaCO_3$ and of cement-rock analyzing 70 per cent $CaCO_3$ are required in a mixture to analyze 75 per cent $CaCO_3$?

$$\text{Percentage limestone} = \frac{75 - 70}{95 - 75} \times 100 = \frac{500}{25} = 20.$$

Percentage cement-rock = 100 — 20 = 80.

To illustrate a case where these formulas are applicable, let us suppose that our hopper holds 10,000 pounds then 10,000 × 0.20 or 2,000 pounds of this must be limestone and 10,000 × 0.80 or 8,000 pounds must be cement-rock.

Formulas for Correcting the Mix

After the mixture has been made and checked, if it is desired to correct that which has been already ground, the two formulas first given, as the case may require, may be used. If the mix analyzes too low and limestone is needed the first formula must

be used. If too high and clay is called for the second formula will give the amount.

Unfortunately in many mills no provision is made for correcting the mix after it leaves the grinders and the efforts of the chemist are directed merely to making the subsequent mix all right. The formula given below is for use here and gives the correct amount of limestone for the new mixture.

4. To calculate the correct percentage of limestone to be added to a cement-rock from the result of a former mixture of the two.

Let—

M = Percentage of $CaCO_3$ desired in mixture.

F = Percentage of $CaCO_3$ found in mixture.

A = Percentage of limestone already added.

L = Percentage of $CaCO_3$ in limestone.

X = Corrected percentage of limestone needed to make the mixture analyze M per cent $CaCO_3$.

Then—

$$X = A + \frac{(M - F)\ (100 + A)}{L - M}.$$

Example 1.—The mixture analyzes 74.5 and should analyze 75 per cent $CaCO_3$. Twenty per cent (of the weight of the cement-rock) of limestone analyzing 95 per cent $CaCO_3$ was added. What amount should be added?

$$X = 20 + \frac{(75 - 74.5)\ (100 + 20)}{95 - 75} = 20 + \frac{0.5 \times 120}{20} =$$

$$20 + \frac{60}{20} = 23 \text{ per cent.}$$

Example 2.—The mixture analyzes 76 per cent $CaCO_3$ and should analyze 75 per cent $CaCO_3$. If 20 per cent of 95 per cent limestone has been added, to what should this be reduced?

$$X = 20 + \frac{(75 - 76)\ (100 + 20)}{95 - 75} = 20 + \frac{-1 \times 120}{20} =$$

$$20 - 6 = 14 \text{ per cent.}$$

Where clay is added to limestone or marl and where formula 2 has been used to calculate the mix then formula 4 becomes as follows:

5. To calculate the correct percentage of clay or shale to be added to a limestone or marl from the result of a former mixture of the two.

Let—

M = Percentage of CaO desired in mixture.
F = Percentage of CaO found in the mixture.
B = Percentage of clay already added.
C = Percentage of CaO in clay.
X = Corrected percentage of clay needed to make the mixture analyze M per cent CaO.

Then—

$$X = B - \frac{(M - F)\ (100 + B)}{F - C}.$$

A slide rule will greatly facilitate rapid calculation of cement mixture and changes to be made in the same.

A 10-inch one can be bought for as little as $1.25 and will be found to come in very handy for other laboratory calculations where accuracy is not required to more than three figures, such as figuring out the percentage of sulphuric anhydride and magnesia in an analysis.

Formula for a Three-Component Mix

When a three-component mix is employed as for example where sandstone is added to supply a deficiency of silica in the shale, the following method of calculating the proper proportion of each element so as to give definite ratios between the silica and the alumina, on the one hand, and the silica, iron oxide and alumina, on the other, will be found convenient and exact.

Let the following represent the analysis of the three components respectively.

	Limestone	Shale	Sandstone
Silica	S_1	S_2	S_3
Oxide iron and alumina	O_1	O_2	O_3
Lime (or carbonate)	L_1	L_2	L_3

Let r and R represent the ratios desired as follows:

$$r = \frac{\text{Silica}}{\text{Iron oxide} + \text{alumina}}$$

$$\text{R} = \frac{\text{Lime}}{\text{Silica} + \text{iron oxide} + \text{alumina}}.$$

Now solve the following:

$$a = \text{S}_1 - r\text{O}_1.$$
$$b = r\text{O}_2 - \text{S}_2.$$
$$c = r\text{O}_3 - \text{S}_3.$$
$$d = \text{L}_1 - (\text{S}_1 + \text{O}_1)\text{R}.$$
$$e = (\text{S}_2 + \text{O}_2)\text{R} - \text{L}_2.$$
$$f = (\text{S}_3 + \text{O}_3)\text{R} - \text{L}_3.$$

The proportions of the three components will then be as follows:

Limestone : sandstone : shale.

$$ec - bf : ea - bd : cd - fa.$$

Or if

Limestone = 100.

$$\text{Shale} = \frac{cd - fa}{ec - bf} \times 100$$

$$\text{Sandstone} = \frac{ea - bd}{ec - bf} \times 100.$$

Example.—Find the proportions in which to mix the three materials whose analyses are given below so that the ratios between the silica and the oxides will be 2 and the ratio between the carbonate of lime and the silica and oxides will be 4.

ANALYSES.

	Limestone	Shale	Sandstone
Silica	2.4	50.2	75.6
Iron oxide and alumina	0.8	32.4	15.4
Carbonate of lime	95.0	4.3	2.2
Carbonate of magnesia	1.8	2.1	2.4

Solution.—

$$a = 2.4 - 1.6 = 0.8. \qquad b = 64.8 - 50.2 = 14.6.$$
$$c = 30.8 - 75.6 = -44.8.$$
$$d = 95.0 - (2.4 + 0.8) \times 4 = 82.2.$$
$$e = (50.2 + 32.4) \times 4 - 4.3 = 326.1.$$
$$f = (75.6 - 15.4) \times 4 - 2.2 = 362.8.$$

Limestone = 100 pounds.

$$\text{Shale} = \frac{(-44.8 \times 82.2) - (362.8 \times 0\ 8)}{(326.1 \times -44.8) - (14.6 \times 362.8)} \times 100$$
$$= \frac{-3.972.80 \times 100}{-19,906.16} = 19.9 \text{ pounds.}$$

$$\text{Sandstone} = \frac{(326.1 \times 0.8) - (14.6 \times 82.2)}{(326.1 \times -44\ 8) - (14.6 \times 362.8)} \times 100$$
$$= \frac{-939.24 \times 100}{-19,906.16} = 47.$$

The above calculations can be made in a few minutes with a slide rule. Mr. L. T. Bachman, chemist of the Santa Cruz Portland Cement Co., has devised for his own use an ingenious system of tables and formulas which reduce to a minimum the calculations required for a three-component mix. These are in constant use at this plant where a shale high in silica is employed in connection with one high in alumina.

Proportioning the Mixture in the Wet Process

For controlling the mixture in mills using marl and clay and consequently the wet process, many methods are in vogue. At some of the plants the slurry is merely dried and the carbonate of lime determined in the usual manner as outlined in Chapter XVII, by titration with standard *N/2* acid and alkali. Another plan and one which was in use in the laboratory of the Omega Portland Cement Co., Jonesville, Mich., is to determine the lime by titration with standard *N/2* acid and alkali, and also "the silicates." The determination of the latter is also given in the chapter on "The Analysis of the Mix." The ratio between the silicates and the lime is then kept constant. In a sample of correctly proportioned slurry upon which this determination was made, the

ratio was 3.8. This ratio undoubtedly will vary at different mills, and also with any variations in the manner of carrying out the determination of the silicates, so that this ratio must be fixed by experience. At a new mill it could be determined to some extent before beginning operations by making up a set of "standard samples" (using the formula given on page 79 to determine the proper proportions) from various lots of marl and clay. The marl for these samples should be so selected as to cover the range expected to be met with in practice. This applies to the clay also. The ratio between the lime and the silicates should then be determined and if found fairly constant it can be adopted. If possible these samples should be checked by burning in a small kiln and examining the properties of the resulting cement. It may be found necessary after starting up the mill to raise or lower this ratio.

At the two mills of the Sandusky Portland Cement Co., the mix is controlled by the ratio between the percentage of lime, determined by acid and alkali, and the percentage of "insoluble," as determined by boiling one gram for five minutes with 10 per cent hydrochloric acid, filtering, washing, igniting, and weighing. This ratio is also different for different works. At the Sandusky plant of the above company the ratio is about 3.9 and at the Syracuse, Ind., mill 4.2, the difference being due to a greater amount of carbonate of magnesia and a more silicious clay at the latter mill. This ratio must be fixed like the lime-silicate ratio by comparison with samples carefully analyzed.

The author has used the following method of control as doing away with the uncertainties due to water and organic matter in clay-limestone mixtures and in slurry: Measure into a large weighed platinum crucible such a quantity of wet slurry as will give about 0.8 gram of dried slurry (or that amount, 0.8 gram, direct of dried slurry). Dry rapidly, avoiding any loss by spattering if necessary, ignite cautiously at first, then strongly for five minutes over a Bunsen burner, and then for ten to fifteen minutes over a blast. The result will be a clinker of practically the same composition as that obtained in the kiln except that it lacks the fuel ash. The crucible and contents are then weighed

and the weight of the clinker calculated. The lime is then determined in this clinker by the rapid permanganate method given in Chapter XVI. This gives an excellent check on the slurry, if the magnesia is anywhere near constant, as it is only necessary to keep the lime in this clinker around a constant figure. The sample of wet slurry may be rapidly dried, in the crucible, in the following manner: Incline the crucible on a tripod over a burner turned low, in such a way that the flame plays under the upper part of the crucible. This will cause a rapid evaporation of the water. When the mass looks dry the burner can be moved back gradually until it plays upon the mass directly and allowed to remain here five minutes when the crucible is ready for the blast. The lime will be somewhat higher in this artificially prepared clinker, than in that from the kilns, owing to the contamination of the latter by the fuel ash, and still higher than the finished cement in which it is lowered by the addition of gypsum and the absorption of water from the air. What the lime should be in the clinker can easily be determined by applying the method to samples of the mixture which have been subjected to complete analysis and found to be of correct composition.

In making the mixture with wet materials such as clay and marl the water and organic matter are disturbing elements. In order to make the mixture with these materials it is necessary to determine the percentage of water they contain, and from this to calculate the weight of wet marl or clay equal to a given weight of dry material. For instance suppose the marl to contain 60 per cent water and the clay 15 per cent. Then 100 pounds of wet marl would only contain 100 — 60 or 40 pounds dry marl, and from the proportion

$$(40 : 100 :: 100 : x)$$

we find 250 pounds of wet marl equivalent to 100 of dry marl.

If 100 pounds of dry marl require 31 pounds of dry clay, it would require 36.4 pounds of wet clay by a similar calculation. So that our proportions would be 250 of wet marl to 36.4 of moist clay.

This will apply to the use of any of the formulas given in this chapter, when used for calculations involving wet materials. The

results will be in pounds of *dry* material and must then be calculated to wet marl, clay or slurry. In using the ratio between either the lime and the silicates or the insoluble, the lime and the silicates must be found in the marl, and the silicates (and lime if any) in the clay, if the first method is used; and the lime and the insoluble in the marl, and the insoluble and the lime, if any, in the clay, if the second method is to be used, in order to proportion the two. The following formula will give the proper proportions of clay and marl to make a slurry of a given ratio.

Let—

L = Lime in the marl.
l = Lime in clay.
S = Silicates (or insoluble) in marl.
s = Silicates (or insoluble) in clay.

$$R = \text{Ratio} = \frac{\text{Lime}}{\text{Silicate (or insoluble)}}$$

Then—

$$\frac{\text{Marl}}{\text{Clay}} = \frac{R \times s - l}{L - R \times S}.$$

This formula may, of course, be used to correct a slurry found to be too high or low in lime. In this event, if the clay is called for, the lime and silicates in the slurry should be represented by L and S, but if marl is needed, by l and s.

Correcting Slurry

Slurry is generally corrected by mixing together two or more tanks of slurry of known composition in such proportions that they will give a mixture of the desired composition. The calculation is, of course, not quite so simple as that for a dry mixture because of the water and the fact that slurry is usually mixed by volume and not by weight. In proportioning two slurries, we need to know the following:

1. Percentage of solids in the slurry.
2. Percentage of lime in the slurry, dry basis.
3. Weight per cubic foot of the slurry.
4. Dimensions of the slurry tanks.

The weight is usually determined by weighing a known volume, or else taken from a table previously prepared showing the weight per cubic foot of slurry of different percentages of moisture.[1] If a table is prepared, this should show the weight of solid matter in a cubic foot of slurry. If no table is used, this is calculated from the percentage of solids and the weight per cubic foot. The proportions of the two slurries on a dry basis are first calculated and having this and the weight of solids in a cubic foot the calculation of the relative volumes to be mixed is then easy.

For example, suppose:

	Tank A Per cent	Tank B Per cent
Moisture	38	40
Solids	62	60
Carbonate of lime, $CaCO_3$	70.2	76.5
Weight per cubic foot	100.3 lbs.	98.4 lbs.
Diameter of tank	25 ft.	25 ft.
Depth of slurry in tank	15 ft.	16 ft.

Carbonate of lime desired in the mixture, 74 per cent

The two slurries if dry would be mixed in the following proportions:

$$A : B :: (76.5 - 74) : (74 - 70.2) :: 2.5 : 3.8$$

or say 250 pounds of A to 380 pounds of B.

Now the solid matter in a cubic foot of slurry A is of course $100.3 \times 62 = 62.18$ pounds and the solid matter in a cubic foot of slurry B is similarly $98.4 \times 60 = 59.04$ pounds. The relative proportions by volume will then be

$$A : B :: (250 \div 62.18) : (380 \div 59.04) :: 4.02 : 6.44.$$

The volume of slurry A to be mixed with slurry B would then be found from the proportion

$$15 : x :: 6.44 : 4.02$$

$$x = 9.4 \text{ feet, or } 9 \text{ feet } 4\tfrac{3}{4} \text{ inches.}$$

Slurry tanks are usually made of the same dimensions in order to simplify calculations. When the two tanks differ in diameter or area of cross-section the calculation must be based on cubic feet and not on depth of tank.

[1] Refer to Chapter VIII for such a table.

Calculating the Probable Analysis of the Cement Clinker

The problem of determining the probable composition of a cement from its raw materials is often put up to the chemist. The solution is by no means easy. The usual rule is to add together the percentages of silica, oxide of iron and alumina, lime and magnesia and to divide this sum into the percentage of each compound, multiplied by 100, for the percentage of that compound which will be present in the clinker. If this rule is followed, the results obtained for silica and for iron oxide and alumina will be too low and the lime much too high unless oil or natural gas is used for fuel in burning. This is because the ash of the coal enters into the composition of the clinker and also because the clinker contains other constituents present in the raw materials which are not volatized in burning: *viz.*, soda, potash, some of the sulphur which oxidizes to sulphur trioxide, carbon dioxide, water, etc.

To accurately calculate the composition of the clinker from the analysis of the raw material is, therefore, impossible, and the best we can do is to assume certain corrections. First of these is for the coal ash entering into the clinker. My own experiments show that in the rotary kiln about one-half the ash enters the clinker. The West Virginia gas slack coal contains about 10 per cent ash on the average. This ash is composed of about 40 per cent silica and about 20 per cent each of iron oxide and alumina. If, therefore, 90 pounds of coal are required to burn a barrel of cement about 15 pounds (equivalent to 1.5 pounds of ash) are required per 100 pounds of raw material burned. Assuming half the ash to enter the raw material, the silica in the latter is increased by $0.5 \times 1.5 \times 0.40 = 0.30$ per cent, and the iron and alumina each by $0.5 \times 1.5 \times 0.20 = 0.15$ per cent.

Analyses of Lehigh Valley clinker when fresh from the kilns show it to contain about 2 per cent of potash, soda, sulphur compounds, carbon dioxide and water combined. Clinker from other localities will probably not vary very widely from this.

Assuming the above corrections, the author's rule for calculating clinker from the mix analysis is as follows:

Add together the percentages of silica, oxide of iron, alumina, lime and magnesia. To the sum add 2.75. Call the result the "Clinker total."

To find the percentage of silica, add 0.30 to the percentage of silica in the raw material, multiply the sum by 100 and divide by the "Clinker total" as found above. The result will be the percentage of silica in the clinker.

To find percentage of iron oxide or alumina add 0.15 to percentage of either as the case may be in the mix, multiply by 100 and divide by "Clinker total," etc.

To find percentage of lime or magnesia, divide percentages of these by "Clinker total," etc.

Example.

ANALYSES OF RAW MATERIAL.

Silica	13.44	
Oxide of iron and alumina	6.54	
Lime	41.84	
Magnesia	1.93	
		63.75
Correction for ash, etc.		2.75
Clinker total		66.50

Percentage of silica:

$$100 \times \frac{13.44 + 0.30}{66.50} = 20.66.$$

Percentage of iron oxide and alumina:

$$100 \times \frac{6.54 + 0.30}{66.50} = 10.29.$$

Percentage of lime:

$$\frac{100 \times 41.84}{66.50} = 62.92.$$

Percentage of magnesia:

$$\frac{100 \times 1.93}{66.50} = 2.90.$$

Probable composition of clinker:

Silica	20.66
Iron oxide and alumina	10.29
Lime	62.92
Magnesia	2.90

When coal containing higher percentages of ash or ash of a different chemical composition than that given above is employed for burning, the chemist using the above as a guide can readily calculate the corrections to be applied.

CHAPTER V

QUARRYING, MINING AND EXCAVATING THE RAW MATERIALS

Limestone, cement-rock and shale are usually quarried, while clay is dug from pits and marl is dredged, often from under water. In a few instances, limestone and shale are mined but fully 85 per cent[1] of the material used in cement manufacture is quarried by open pit methods. Mining is only employed where the overburden is so thick that stripping cannot be done economically. Marl often lies under water and here dredging must be resorted to. There are some beds of dry marl, however, which can be worked by the ordinary pit methods employed for digging clay. Notable examples of this are in the marl beds around Sandusky, Ohio.

Quarrying the Stone

Some deposits of cement-rock and limestone are so situated that they can be opened along the hillside. At others, it is necessary to go down. When a deposit is opened on the side of the hill, the cars can usually be run to or from the latter at a slight grade. At the plant of the Bath Portland Cement Co., Bath, Pa., where cement-rock is quarried in the side of the hill, cars are run down by gravity, dumped, then elevated to a trestle by mechanical means and run back to the quarry by gravity.

The methods pursued in quarrying are governed by the physical characteristics of the deposit, the chemical composition of the rock and the amount of overburden to be taken off. When the rock permits, deep faces from 30 to 150 feet are employed as these are more economical than shallow ones.

When the beds are flat, the face of the quarry may be in any position desired and is here governed chiefly by convenience with regard to transporting the rock to the mill. For beds which are steeply inclined, better results are obtained by having the face run at approximately right angle to the strike of the beds and so cut across them. This gives a more uniform

[1] "Rock Quarrying for Cement Manufacture," by Oliver Bowles, *Bul. 160*, U. S. Bureau Mines.

material, as all the beds are quarried at one time and are not encountered one after the other as would be the case if the face ran parallel to the strike. It is also very difficult to quarry in the latter position. Where the pitch is slight the face may be run parallel with the strike. If this is done, it should move up with the beds and not down with them, as better drainage, etc., is secured, cars can be moved away from the face by gravity and a better quarry floor can be obtained. It is also easier to blast the rock down hill than up.

In quarrying, surface water has to be taken care of. With quarries on the side of a hill, it is only necessary to provide drainage ditches. Where the quarries are run straight down, however, a sump is usually provided into which the water is drained and from which it is pumped by means of electrically driven centrifugal pumps, or else steam or air driven plunger pumps. Unless the quantity or lift is excessive, the taking care of the water seldom figures very materially in the cost of quarrying.

Stripping

All the materials mentioned are usually covered with an overburden which is called "stripping." Whether this material must be removed or can be quarried with the material underneath depends on the chemical composition of the stripping. Where it is clay and the underlying rock is limestone, it can often be used in the mix, taking the place of so much clay or shale. Occasionally, however, from the sand or other characteristics of the stripping it cannot be so employed and in this case it must be removed before the rock is quarried. This is usually done by hand loading, with small steam shovels, or by a drag line excavator.

Where the stripping amounts to only a foot or two, it is quite common at cement plants employing limestone and clay to blast down this overburden with the limestone and to load and send it to the mill with the latter. There are many cases, however, where this cannot be done. As stated, the chemical composition may be such that the overburden is an undesirable constituent

of the mix, or even if of correct composition, the quantity of overburden may be too great to balance the quantity of limestone underlying it. The overburden usually consists of clay and it is difficult to crush this with the rock during wet weather.

If the overburden could be intimately mixed with the stone, there would generally be no objection to its being blasted down with the stone. Unfortunately this result cannot be obtained and the overburden usually lies over part of the rock only. In dry process plants, in which the facilities often are not very good for controlling the mix, it may increase the latter difficulty to mix the stripping with the limestone in the quarry and it will in such cases be advisable to strip off and carry it to the mill separately.

Cement-rock is generally stripped in the Lehigh District due to the fact that if the clay is allowed to go in with the cement-rock the quantity of limestone which must be used with the latter is greatly increased, and consequently the cost of manufacture made higher, since limestone at most mills in this district must be imported from a distance.

Blasting

Formerly, limestone and cement-rock were blasted down in benches, sometimes along the whole face of the quarry and again only a small part of a bench at a time. The drill holes for the blast were usually made with tripod drills operated by steam and compressed air and were seldom carried to a depth of over 16 feet. The objection to this method of blasting was that it was necessary to clean the benches in order to set up the drills. There was also considerable danger to men working on the various benches. Of late years, practically all cement quarries which could adopt the system, have employed the "big blast" method of quarrying and instead of blasting the rock down in benches are now throwing down the whole face, often as much as 200,000 tons of rock at once, the object being to save clearing off of the benches and the trouble of setting up small drills, and to secure greated efficiency in blasting and to promote safety.

The drilling for these big blasts is done by means of "well" or "churn" drills. These may be operated by either electricity, steam or gasoline and are usually self-propelling. In using these drills, holes 6 inches in diameter extending downward from the top of the rock to a few feet below the quarry floor, and from 16 to 20 feet back from the quarry face are sunk. Often, two rows of holes are employed, in which case the second row of holes is from 12 to 15 feet back from the first and the holes in the two rows are staggered. These holes are then loaded with dynamite and all holes are fired at once.

With a good drill from 3 to 7 feet of rock can be drilled per hour depending on the hardness of the rock, its freedom from seams, etc. The quantity of dynamite required for blasting is usually equivalent to one pound of 40 per cent straight nitroglycerine for 3 to 5 tons of rock, with 4 tons as an average. The explosive should be selected to suit the rock and particularly with a view to bringing the rock to such a size that it can be loaded easily and handled by the crusher at the mill. Small jack hammer drills are commonly employed to break up those pieces of rock which cannot be handled by the shovel or the crusher.

Tripod drills are still used in some cement mill quarries. Where the rock face available is small or where the deposit consists of thin seams that are full of clay they are more satisfactory.

Loading

In practically all cement mills at the present time the materials are loaded by means of steam shovels. These are usually 60 to 120-ton shovels having one and three-fourths to six-yard dippers. Smaller shovels three-fourths to two yards are used for clay and shale. The large shovels are generally operated on tracks. The "Crawler" or "Caterpillar" type shovel, however, which requires no tracks gives excellent service where the quarry floor is firm, as is usually the case with limestone. (See Fig. 4).

The steam shovel has several advantages over hand loading aside from cheapness. It can load larger pieces of stone and

hence reduces the cost of blasting. It can also load more rapidly, and it is hence easier to keep the mill going with a shovel than with hand loading. From the chemical standpoint, shovels have two big disadvantages. They localize the quarry to a few particular spots and hence unless the rock is very uniform the composition of the material sent to the mill may vary from time to time. There is also no opportunity with the steam shovel to sort out any undesirable material, as can be done by hand.

The "big blast" and steam shovel loading have decreased materially the cost of quarrying stone, but they have also increased the difficulties of the chemist. The big blast throws down the entire vertical face of the quarry in one heap. If it served to mix the various beds intimately it would be an advantage. Unfortunately the opposite is generally true and the beds remain almost as separate, but not as well segregated, after the stone is blasted down as when in the position left by nature. In the case of the old methods of quarrying by means of 16 to 20-foot benches, the beds were usually blasted down in some sort of order and could be quarried uniformly. The steam shovel confines the stone supplied the mill to that obtainable from one or two points in the quarry, while with hand loading the stone can be obtained over almost the entire area of the quarry.

Glory Hole Method of Quarrying[1]

The so-called glory hole method of quarrying has been tried in a few cement works quarries, but has never come into any extended use in these. In this method, a tunnel is driven into the ledge near its base, at a point conveniently situated with regard to the mill. A large chamber is blasted out at the inner end of the tunnel, which is used as a storage bin for the rock to be removed from above. A slightly inclined shaft is next driven up to the surface and the rock is quarried around this shaft in a circle of gradually increasing size and passed down through the opening into cars in the tunnel, the flow of rock being controlled by means of gates.

[1] Bowles, *Bul. 160,* U. S. Bur. Mines, p. 115.

Fig. 4.—95 ton Bucyrus steam shovel.—Edison Portland Cement Co.

Fig. 5.—1-yard Bucyrus dredge.—Coldwater Portland Cement Co.

Mining

It was quite common in the early days of the natural cement industry in the Rosendale region of New York to mine stone, and at a number of cement works to-day the overburden above the limestone is so extensive that it has been found cheaper to mine than to quarry the stone. The mining of stone is more expensive than quarrying under ordinary conditions, but it has some advantages. No stripping has to be done, operations are not interfered with by inclement weather, there are rarely clay seams or pockets to be avoided and a particular bed of limestone can be followed at will. Most limestone mines drift in from the surface and follow practically flat veins. The drilling is done by means of tripod drills. Often a considerable face can be worked, in which event steam shovel loading is possible. As a general thing, however, the loading is done by hand.

Timbering is never resorted to in limestone mining, the limestone itself forming the roof. Pillars of rock are left to support this. In estimating the tonnage of rock available in a deposit which must be mined allowance must always be made for these. Cement plants at Ironton and Superior, Ohio, Independence and Hannibal, Mo., Manheim, W. Va., Richard City, Tenn., and Oglesby, Ill., mine all or part of their raw materials.

Excavating Marl

Marl as has been said carries considerable water and the deposits usually lie in depressions and often underneath the surface of a shallow lake or marsh. In some instances, the marl deposit is overlaid by a foot or more of peat which must be dredged off. In excavating the marl several plans are followed, one of the most common is that of a steam dredge mounted on a barge which scrapes up the marl from the bottom of the lake and loads it on barges. These barges are then towed to the wharf and unloaded by machinery on belt conveyors which carry the marl to the mill. This can, of course, be done only where the marl lies under water. When the beds have been drained, it is usual for the steam dredge or shovel to float on its barge, in the channel which it cuts out of the marl, and to load the marl on to cars,

running on temporary tracks, on a bank by the barge. The channel fills with ground water and the bank is thrown up by the dredge either from the stripping on top of, or the material underneath the marl. Instead of using barges and cars to convey the marl to the mill, some of the Michigan mills drop their marl from the scoop of the dredge into the hooper of a pug mill on a boat or car. Here the marl is mixed with water to form a

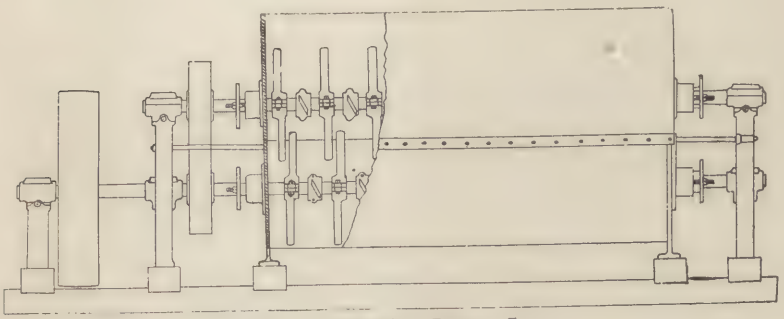


Fig. 6.—Pug Mill.—Bonnot Co.

thin mud, which is pumped to the mill through a pipe line, carried over the marsh or marl bed on a wooden trestle. The steam dredges are of the same type as those used for deepening the channels of rivers and harbors. They consist of a scoop or dipper having a hinged bottom and fixed to a long arm. This arm can be swung to either side, raised, lowered or pushed forward, by a system of chains, racks and pinions. Some of the dredges are of the orange peel and some of clam shell bucket type. These have a bucket hanging from a revolving arm by cables or chains, which opens and shuts and is filled by lowering open to the bottom of the lake and then closing. Fig. 5 shows a steam dredge such as is used in excavating marl.

The pug mills, Fig. 6, used in cement works are similar to those used in the better equipped brick yards, and consist of a long steel cylinder, in which revolve two shafts provided with steel blades. The wet marl enters at one end and is forced out at the other. During its passage it is churned up by the blades and thoroughly mixed. When the marl is pumped from the

lake to the mill, it is often necessary to locate a separator on the barge to take out the sticks, roots, etc. This generally consists of a perforated screen through which the marl is forced. The separator also serves as a pug mill in reducing the marl to a uniform paste.

Marl is usually pumped to the mill by centrifugal pumps. Any of the pumps or systems used for handling the slurry of the wet process however may be used for pumping marl.

Digging Clay and Shale

As clay is soft the steam shovel can both dig out the clay and load it on the cars. Usually it is necessary to carry the clay some distance, for the mill is always located as near the marl or limestone as possible, as four or five times as much of these are used as of clay or shale. Clay can generally be dug without blasting but shale usually has to be broken up by means of drilling and dynamite or black powder. Both clay and shale are occasionally mined.

Haulage

The method of transporting stone to the mill and the type of cars employed differ with the mill and are influenced by many conditions such as the distance of the deposits from the mill, the relative elevations of the crusher and quarry floor, whether hand or steam-shovel loading is employed, etc. Where the quarry is some distance away from the crusher, the cars are usually drawn to the crusher by a steam, gasoline or electric locomotive; and in this case the preferable arrangement is one where the whole train of cars may be passed over or to one side of the crusher, as the case may require, and the cars then dumped of their load in order. Where the elevation of the crusher is such that this arrangement can not be employed, the cars are generally disconnected from the train in order and pulled one at a time up to the crusher by a steam or electrically driven drum hoist. This same system is employed where cars are to be drawn up out of a pit quarry adjacent to the mill.

Where hand loading is practiced the cars are usually small (of 2 to 4 tons capacity each) and should set low on the track in order to facilitate loading. Fig. 7 shows an excellent form of

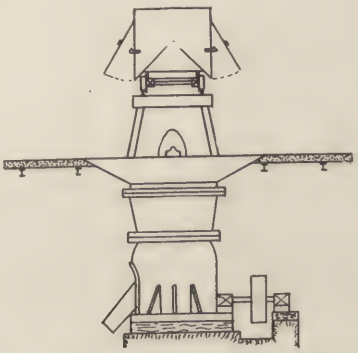


Fig. 7.—Common arrangement of track and crusher for hand dumping of cars.

car for hand loading and for narrow gauge track. The "V"-shaped, rocker dump, cars so extensively employed by contractors are also used to some extent. With the gabled bottom car shown in Fig. 7, the track usually straddles the crusher and when the car is dumped the rock falls on both sides of this. This is desirable where a gyratory crusher is employed. These cars also stand low on the track allowing easy hand loading as the men do not have to lift the rock so high in order to get it into the car. They are not well adapted to steam shovel loading, however, as the big rocks are likely to break the peak of the gable. They require to be dumped by hand which is also a disadvantage. Figure 8 shows a car which is well adapted to hand loading and to narrow gauge tracks. The body sets low and the projection beyond the wheels gives good capacity to the car.

Figures 8 and 9 show types of cars which are well adapted to both hand and steam shovel loading and which can be arranged to dump automatically. This usually saves at least two men and sometimes more. In both instances, the cars are end dump cars. In both these forms the door of the car is held shut by means of

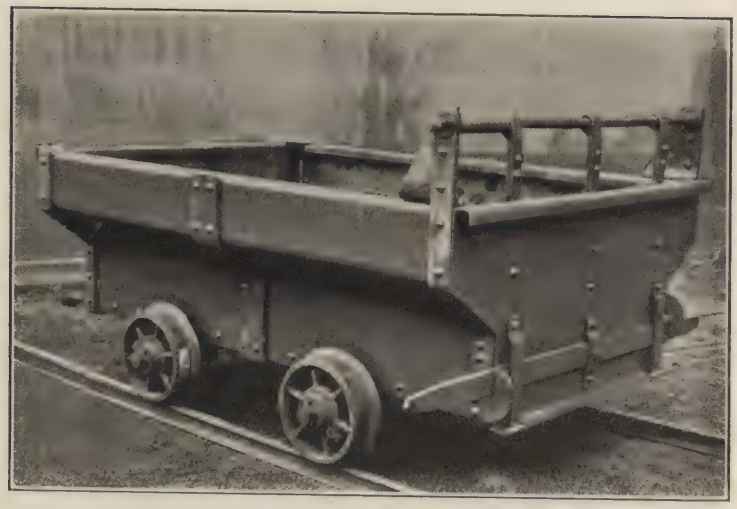


Fig. 8.—End dump car with hinged door, suitable for hand loading and narrow gauge tracks.—Easton Car & Conc. Co.

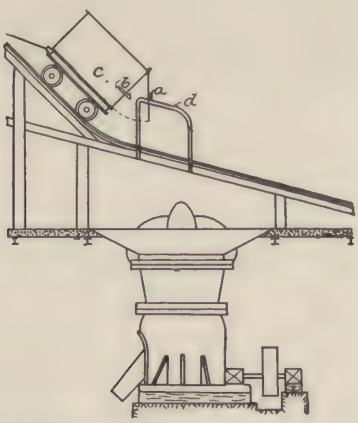


Fig. 9.—Automatic system of dumping cars.—Allentown Portland Cement Co.

a bar, *a*, see Fig. 9, working on a pivot at about the middle of the door face. This bar extends a little beyond the sides of the car and drops into a catch, *b*, bolted to the side of the car, thus securely fastening the door. When the car coming up the incline reaches the proper dumping point above the crusher, the part of the bar projecting beyond the car slides over a rack, *d*, at the side of the track and as the car moves further up the incline the bar is lifted out of the catch by the pitch of the rack allowing the door to be forced open by the weight of the rock against it.

In Fig. 10 the door is held shut by a V-shaped arrangement of bars on the sides. The apex of this V is pivoted at about the

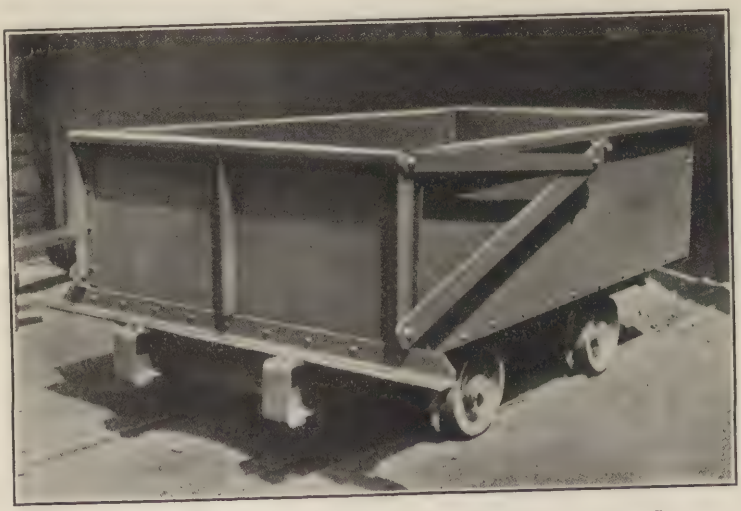


Fig. 10.—End dump car with lifting door.—Easton Car & Conc. Co.

middle of the sides. An angle iron is fastened to the bottom of the door and projects out beyond the sides of the latter. This bar comes in contact with a rack similar to that shown in Fig. 9 and the door is lifted allowing the rock to fall out. In either of the forms shown if used for steam shovel loading the door space must be sufficient to allow any stone which the shovel will handle to pass out this way.

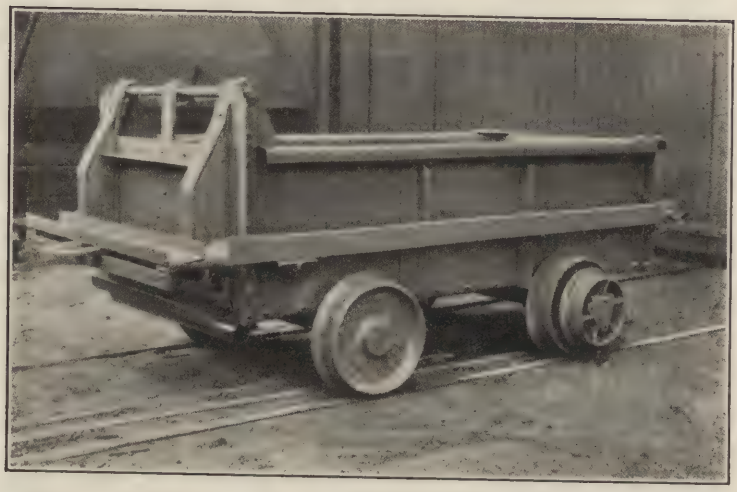


Fig. 11 A.—Car with hinged door arranged to dump through forward end.—Easton Car & Conc. Co.

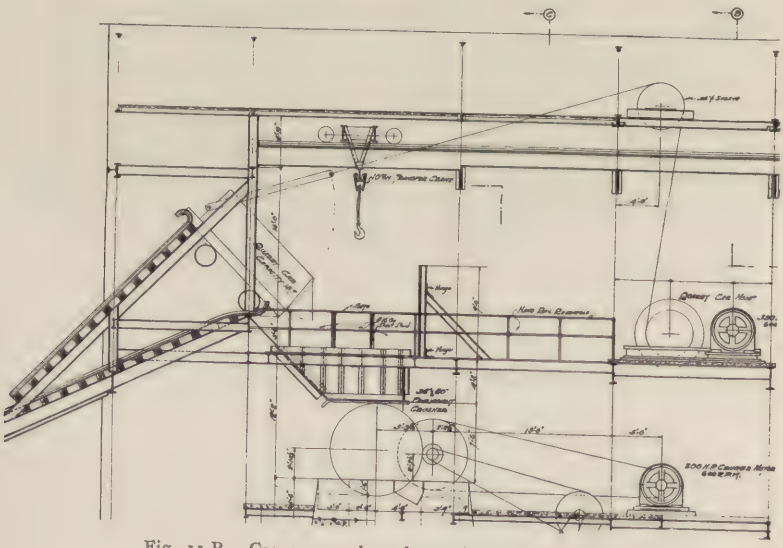


Fig. 11 B.—Car arranged to dump through forward end.

Still another form of car and dump is shown in Fig. 11A and 11B. This is also an end dump car. In this case the door is held shut by a bail, *a*, pivoted to the rear end of the car. The cable used to hoist the car is attached to this bail. There is also a pair of outer wheels, *c*, attached to the rear end of the car, these wheels engage in an outer track and serve to lift the rear end of the car. As this rises, the bail also lifts away from the door allowing the latter to open. Sometimes the wheel, *c*, is attached to the same axle as the rear wheels of the car, sometimes these wheels are cast with an outer tread of somewhat smaller diameter and sometimes these wheels are on a separate axle fastened to the end of the car (Fig. 11B). This car is excellent when skip hoisting is employed, but the bail is troublesome if the cars have to be made up into trains.

Fig. 12.—Popular type of side dump car for shovel loading.—Easton Car & Conc. Co.

When cars are made up into trains and run to the side of the crusher with a locomotive, side dump cars are employed. These may be of the "rocker dump" type or of the "square box" type. When hand dumped the rocker cars are usually employed because

these can be more easily tipped. When air lifts or electric hoists are employed for dumping the cars, the square box cars are probably the best. These may be of the type shown in Fig. 12 in which case they are little more than a square box or skip with sloping sides on a truck and they are dumped by lifting one side by means of a chain ending in a hook which latter engages in an eye on the side of the car. The chain may be operated by either an air hoist or an electrically driven drum winch. Sometimes the cars are pivoted in the middle and have hinged sides or sides which raise.

CHAPTER VI

OUTLINE OF THE PROCESS, MIXING THE RAW MATERIALS AND CHEMICAL CONTROL.

Wet and Dry Processes

Two processes are employed for the manufacture of cement, known respectively as the *wet* process and the *dry* process. The wet process is the older of the two and is used almost universally in Europe. The dry process originated in America and is employed to the greater extent here. The two processes differ only in the treatment of the raw materials and very much the same equipment is used in each.

In the wet process, the limestone and clay (or marl and clay) are crushed, mixed with water, ground and burned wet. In the dry process, the raw materials are crushed, dried, ground and burned. The treatment of the clinker is the same in both processes. The wet process is always used for marl and clay, and the dry process for cement-rock. Both processes are used for limestone and clay, shale or blast furnace slag. Where applicable, the dry process is the most economical, but it is easier to control the chemical composition of the cement by the wet process. This latter is also best where the materials can not easily be dried. It is often stated that the wet process requires less power for grinding, but this point is in dispute.

In the dry process, the limestone, cement-rock and shale are quarried. They are usually crushed to about 2 inches and smaller and dried. The dried materials are stored in large bins and are drawn out of these as desired and mixed in proper proportions by automatic scales. The mixture is then ground and burned. Sometimes the storage and mixing precede the drying, and again the two materials are mixed before crushing.

Where the wet process is employed for limestone and shale, the two materials are quarried, crushed and stored without drying, just as in the dry process. They are then mixed in proper proportions and fed to the grinding machinery, at which point

water is added and the materials ground wet. The result is a thin mud, or *"slurry"* as it is called, which is made just fluid enough to flow easily. This slurry containing from 35 to 40 per cent water is fed directly into the kilns and burned. Where clay is used with limestone it is sometimes treated as above. More often, however, the clay is mixed with water in a wash mill and the thin slurry so formed is mixed with the limestone as it enters the first grinding mill.

Marl if dredged is often simply mixed in some form of pug mill with enough water to give it fluidity, passed through a screen to separate sticks, stones, etc., from it and pumped through pipes to the mill. Here it is stored in large tanks or basins which are continuously stirred. The clay is treated in a wash mill as previously described and mixed with the marl in the tanks.

Importance of Chemical Control

The starting point in the manufacture of cement of uniform high quality is largely one of absolute control of the chemical composition of the mixture fed to the kilns. Occasionally a plant is met with where the raw grinding or burning equipment is insufficient, but for the most part the failure to control the chemical composition of the mix is responsible for any irregular quality of the product.

Chemical analysis of the cement does not always show the trouble particularly when this analysis is confined to a sample representing a large quantity of cement, such as a bin of several thousand barrels or a day's run, because such a bin of cement may be the average of several hours of very high-limed and consequently unsound cement mixed with several hours of cement low in lime; the average of the two being often near the desired chemical composition but the physical properties of the resulting cement having something of the undesirable characteristics of both the high-limed and low-limed clinker.

Such a result is quite apt to occur in the dry process where chemical control is generally a matter of examination of a mixture already made rather than of two materials about to be mixed, as explained below. The routine tests of the dry mill

laboratory are usually *post mortems* rather than *diagnoses* and are of no value so far as correcting the composition of the particular lot of raw material under examination is concerned, but serve only as a guide to the making of succeeding lots.

By far the larger number of mills, both wet and dry, control their mix by means of what are in the industry designated as "readings." That is, samples of the mix are drawn from the grinding mills at stated intervals of time and in these samples the carbonate of lime is determined. If this is found to vary from the desired standard, no correction can as a rule be made in that portion of the mix which has already been prepared, and the test serves principally as a guide to the proportioning of succeeding lots, etc. When the mix is controlled by such a process, the chemist finding his mixture too high or too low in lime (as shown by the reading) decreases or increases his limestone to correct his proportions. In the dry process, this often has the effect of sending the composition to the opposite extreme, with the result that while his low-lime and high-lime clinker will, when mixed, average properly very little of it is *per se* of correct composition.

In the wet process, however, an opportunity is generally given to mix the whole lot of ground material by combining the contents of several slurry basins in one large kiln feed basin, and in this way the averaging is done before the kiln is reached and hence the clinker is of correct composition.

At many dry process cement plants, the question of chemical control is largely one of good judgment on the part of the chemist rather than of chemical test. For example, let us cite the case where a limestone and shale plant is supplied with rock by one large steam shovel. The shale is regular but the various strata of limestone differ much in chemical composition. Added to this variation is also the fact that 3 or 4 feet of clay overlying the limestone is not stripped from the latter but is blasted down with it. Deep well drills are used and the shots are large, each representing several months' supply of stone. All stone is sent direct from the shovel through crushers into a relatively small storage bin and the mix is controlled entirely by "readings" taken

from the tube-mill discharge. Let us suppose, as frequently happens, the shovel is working in the morning on clean limestone comparatively free from stripping. At noon, it encounters a limestone mixed with stripping, and by night it has worked through the stripping and is back on the clean stone. What happens to the mix is this—Sometime during the afternoon the sample drawn from the tube-mill shows the mix to be overclayed and the chemist accordingly decreases the shale. The orders to make this change probably reach the raw mill about the time the shovel reaches clean stone again, with the result that the next sample drawn from the tube-mill will show the mix overlimed, etc. At this mill, the mix would generally be wrong but for the visual inspection and good judgment of the chemist. This condition is by no means unusual and while probably not existing often in quite such an exaggerated form, does occur at times in a more or less modified form at many mills.

Chemical Control

The raw materials sent to the mill usually differ materially from time to time in chemical composition. In the case of limestone and cement-rock this is due to variations in the composition of the stone itself and also to the amount of overburden mixed with the stone.

Usually the shale or clay whether obtained by means of shovels or hand labor, is of regular composition. Sometimes with clay the moisture content needs careful supervision. A few mills use a calcareous shale in which the lime content varies over quite a range. The use of such shale always greatly complicates the problem of controlling the chemical composition of the mix by introducing two variables instead of one.

The influence of occasional variations in the composition of the raw materials are designed to be taken care of at most plants by storage bins of varying forms and sizes.

The employment of a large stone storage divided into two or more bins seems to be the most feasible method of securing a uniform raw material. In many instances, however, such stone houses are poorly designed. If we place rock continuously on

the middle of a pile and draw at the same time below from the center of this, we will obtain pretty much the same stone that is being delivered to the pile and very little if any mixing will occur. Even where the discharge is not directly under the point of filling this flow of material between the two points occurs. In designing a stone house, therefore, this should be divided into at least two bins but I do not think anything is gained by numerous small tanks or bins.

Another action which should be kept in mind is the so-called segregation of materials in the bins. If a mixture of coarsely crushed limestone is fed from an overhead source into the center of a pile, it will be found that the coarse material will roll to the outside of the pile while the fine material will lie where it falls. If the pile is tapped from the center, the first material drawn is almost entirely the fines, while the coarse material is the last to be obtained. As the fine material usually contains the stripping and is always lower in lime than the coarse material, it will be seen that the composition of the material obtained when the pile is first tapped will be much lower in lime than that of the last portion obtained.

Another fact which should be borne in mind, is that the finer the rock is crushed, the better mixture will be obtained and the less segregation will occur in the bins. For this reason it is best to crush the materials as far as practicable before storage.

Two methods of determining the composition of the raw materials before mixing are in common use, one is to place the crushed material in a bin and to analyze a sample representing the contents of this bin, the other is to analyze a sample taken of the materials in the ground. In the former method, the mixing is done by drawing from previously analyzed bins of the two materials. In the latter, the mixing is usually done at the crusher. Occasionally, however, bins are used and the quarry analysis is taken as that of the contents of the bin. In the case of bin sampling, the sample is usually drawn by means of some form of automatic sampler. In the case of quarry-sampling of limestone, cement-rock or shale, the "mud" or ground material removed from the drill holes is employed. Often auger holes

are employed for sampling clay before digging, the material removed by the auger constituting the sample.

Very often, however, the mixing of the two materials is done without previous analysis by the "Reading Method," which as previously stated consists in mixing the two materials according to the results from a determination of the carbonate of lime in the mix after this has been ground in the mill. As the process is a continuous one and determinations of the carbonate of lime are made every few hours the composition of one lot of mix determines the proportions of the two materials to be used in succeeding lots. In spite of the fact that it is apparently much the less scientific of the methods available, the reading method will usually give better results than the other two. This is because of the difficulty of properly sampling material in large pieces mixed with fines and intermediates.

The only method of sampling such material which will give accurate results is some system of crushing and quartering in several steps such as is used for ore sampling, and this would involve an expensive sampling plant. As an illustration of such a plant, let us suppose that the material came from the crusher on a pan conveyor. Arrangement could be made to trip every tenth bucket into a small crusher which would crush to say 1 inch and under. The discharge from this crusher would then be sampled and the sample crushed to say one-fourth inch. This one-fourth inch material in turn would be sampled and the sample crushed to 10-mesh. The fine material could then be sampled and this final sample ground to the necessary fineness for analysis. It will be seen that such an arrangement would involve handling quite a lot of material.

In a cement plant using 1,000 tons of stone per day, the first sample would amount to 100 tons to be crushed to 1 inch, the second to 10 tons to be crushed to one-fourth inch, the third to 1 ton to be ground to 10-mesh and the fourth to 200 pounds to be ground to laboratory fineness. It is doubtful if accurate results could be obtained with much greater fractions.

Mixing the Raw Materials

The raw materials go from the quarry to a crusher or stone house. Here they are treated in one of several ways:

1. This method is now obsolete and is only employed by a few of the older mills. It is applicable only to cement-rock. The cement-rock and limestone (or clay) are dumped directly into large piles, which are then analyzed, and from this analysis the necessary proportions are calculated. The rock is then loaded on buggies or barrows and wheeled to the crusher after being weighed, where it meets another buggy or barrow loaded with the calculated amount of limestone (or clay). The two barrows are then dumped into the crusher together, or one after the other. In some mills using cement-rock and limestone of nearly the same composition the materials are not even weighed before being dumped and the barrows are merely averaged as holding so much, the proportions being roughly made somewhat in this manner: two barrows of rock to one barrow of limestone, etc. This system is not satisfactory on either the score of correct mixing or economy of handling—the former from the obvious difficulty of sampling such an irregular material as cement-rock and the latter because of the extra handling of the rock and limestone.

2. The cement-rock or limestone may be weighed in the cars as it comes from the quarry and the proper amount of limestone or clay, as calculated from the quarry analysis or readings added. The method of adjusting the proportions varies at different mills. With cement-rock and limestone it is often only necessary to regulate the number of cars of each going to the crusher, the weight of material in the cars being supposed to average. This method of mixing is sometimes possible with shale and limestone, particularly if the shale is calcareous and consequently the difference between the two materials is not so great. When more accurate amounts of the two material are required, this system is sometimes employed but the weights of material in the cars are adjusted. Occasionally the limestone cars are weighed and a weighed amount of shale or clay is dropped on top the lime-

stone or added at the crusher from an overhead bin. The materials are then crushed together, part of the stone going to the mill and part of it being stored in bins for the night. The mix is drawn from the bins when desired upon belt conveyors running to the mill.

In this system if the materials are limestone and clay and they are dumped into a bin, the two are liable to separate, the clay remaining at the center of the pile and the limestone rolling to the edges with the result that when the pile is attacked from the center the clay is first obtained and then the limestone. This, of course, gives a very irregular mix. This system is most applicable for limestone and cement-rock, although even here some separation of the materials takes place in the bin, but it gives a much more regular mix than would result from its use with clay and limestone. Generally speaking, it is never satisfactory to dump a mixture of two dissimilar materials into a large bin unless the mixture is first granulated.

3. The materials are crushed separately and conveyed into bins, each material having its bin or series of bins. The two materials are then drawn out of the bins as required and mixed in the desired proportions by automatic or hand scales. The proportioning of the two materials is determined by analysis of quarry samples, bin samples, or "readings" taken from the tube mill discharge. This system is now generally employed by mills using limestone and clay or shale and in both the wet and dry process.

4. A better way then any of the above, is to pass the shale and limestone through the ball mills or other preliminary grinders, store in separate bins of six or more hours' capacity, analyze each bin and then make the mixture of the two accordingly. This is a particularly desirable way, in the case of a clay and limestone mixture, as segregation of the two can not occur after mixing as both are finely ground and the mixture of clay and limestone is a homogeneous one. An advantage this system has over the one just mentioned is that it is much easier to sample the materials accurately either by hand or an automatic sampler

when in a partially ground condition and also that it is easier to weigh material in such state by means of automatic weighing machines. This system requires at least three bins for each material, one of which is to be used while the other two are filled and analyzed respectively.

A modification of the above system which has been tried and found satisfactory at a number of plants consists in mixing the raw materials before or after being crushed in such a manner that the composition is slightly higher in lime than is desirable. This mixture is then passed through the ball mills or other preliminary grinders and into steel bins holding several hours' run. The material is automatically sampled as passed into the bins, and when the bin is filled, the sample is analyzed and the small amount of dried and ground shale or clay necessary to bring the mixture to the proper composition is then added. Three bins will be needed for the mix and one for the shale.

5. In the wet process, where clay and shale are used, it is considered best to crush the limestone separately and convey this into storage. The clay is then mixed with water and worked into a thin slip in a wash mill. The limestone is drawn from storage as required and passed to the bins above the grinding mills. The latter are equipped with automatic feeders which feed the mills at a regular and uniform rate. The clay slip is added to the limestone just before the latter enters the grinding mill, the proportion of clay being obtained by an automatic feeder of the "Ferris wheel" type such as is used for feeding slurry to the kilns (see Chapter XI), or else by a needle valve. The two materials are then ground together.

Correcting the Mix

In wet-process plants, the fully ground slurry usually passes from the grinding mills to what are known as "correcting tanks." There are usually at least three of these and often six or eight. One tank is filled at a time and after filling a tank a sample of the slurry in this is carefully drawn and the necessary determinations made on this (usually water and calcium carbonate). In

the older wet process plants, provision was made for adding ground clay or marl as desired to the slurry before this went to the kilns. To-day, however, when necessary to correct the mix this is done by mixing the slurry from two or more correcting tanks, the mixing being done in the kiln feed basins. These are made large enough to hold the contents of two or more correcting tanks. Both the correcting tanks and kiln basins are provided with agitators and their contents are stirred continually by these so that no separation can occur. These agitators also serve to mix the slurry thoroughly.

For correcting the slurry, the chemist will usually aim to have on hand one tank of material which is a little higher in lime and one which is a little lower in this constituent than is set as a standard. These are used to correct by mixing either with each other or else with a third lot, etc., as indicated. The proportions are determined by volume and usually by drawing off so many feet of slurry from each tank, the latter having been previously calibrated. (See page 91).

In the dry process, few mills are equipped with any means for correcting the mix after this is once fully ground, although at many mills this adjustment is partially secured by the storage of the ground material in large bins. These serve to equalize the composition by averaging a day or more's output of the raw mill.

At the dry process plant of the National Cement Co., Montreal, Quebec, Canada, of which the author is the engineer, the following system of "blending silos" is provided for correcting the ground mix before this goes to the kiln. Here the ground raw material goes to one of six concrete silos each 15 feet in diameter by 53 feet high and holding raw material for 1,200 barrels of cement each. The mix is sampled automatically as the tanks are filled. Each tank is provided with four openings and the amount of material fed out of the silos can be regulated within quite wide variations. These silos serve to correct the mix by blending two or more tanks as the pulverized material is sent to the kiln bins, the mixing being done by the screw conveyors used to carry the material. Fig. 13 shows these blending silos.

The author suggests the following as an ideal method of mixing the raw materials and correcting the composition of the ground mix. Assuming that the grinding would be done in two stages he would suggest making an approximate mix at the crusher or before the grinding and the use of two sets of tanks or bins. One set of at least four, and better, six or eight tanks to be placed

Fig. 13.—Blending silos for ground raw material.

after the preliminary mills (Hercules or ball-mills) and one set of four or more after the secondary mills (tube mills). The tanks in the first set should be sufficiently large to take care of at least four hours' run of the mill. Each system should be provided with an automatic sampler so that the contents of each tank could be sampled as ground. Where ample rock storage has been provided to give fairly uniform rock, the four tanks could then be used in this manner. One tank would be filling, the second tank would be under test and the third and fourth tanks would be used

straight, or mixed if necessary to give the proper composition. When analysis proved a tank to be of incorrect composition it would be necessary to so proportion the next tank that the two could be mixed so as to give a mixture of correct composition. The second set of tanks would receive the fully ground material. They would serve as a further means of correcting the mix when necessary by blending the contents of two or more tanks as the pulverized material is sent to the kiln bins as explained above.

At some plants, it would no doubt be found most convenient to use such a series of tanks for mixing. That is, to grind the materials separately to 10-20 mesh before the mixing is done. In this case, certain tanks would be set aside for limestone and certain tanks for clay, and both materials would be sampled automatically and mixed according to the analysis of these samples. It is comparatively easy to secure an accurate sample of 10-20 mesh material, while it is extremely difficult to obtain anything which will properly represent material crushed only to 1 inch. So that this system of sampling, analyzing and mixing will do with 10-mesh material, but will not give satisfaction with 1-inch material. The statement that the finer the material, the easier it is to sample accurately will hold good for all materials.

No doubt various modifications of this system could be devised to suit local conditions. For instance, at certain plants it might be found best to mix partly by analysis and then to do the correcting by adding to the contents of the tanks as drawn a small amount of clay or limestone ground to 10-mesh.

Storage of the Raw Materials

The mechanical equipment of the stone house consists of the crushers, and in the case of a dry-process plant of driers also. This equipment will be described in the next chapter.

After crushing the rock may be either stored or dried. When the rock is stored in piles uncrushed as it comes from the quarries, it always passes direct from the crushers into the driers, in which case no bins are usually placed above the driers and the rock is fed to the driers as it comes from the crusher, by means of a bucket elevator or a belt conveyor.

When the rock is to be stored in bins after crushing, this storage may be done either before or after drying. With some materials clay for instance and some shales, drying must always come before storage in bins. If this is not done, the more or less damp materials will pack in the bins and can not be drawn out of them by means of spouts.

The storage bins may be of wood, steel or concrete, preferably the latter. When wood is used, this has to be braced from the inside and these wooden braces often are worn away by the rock sliding over them and even broken by the weight above them. Wood, while cheaper in first cost, is unquestionably the most expensive in the long run and indeed from the fire risk is no longer considered in the construction of plants which represent an investment of a million or more dollars.

Circular reinforced concrete or steel tanks are much used for stone storage. These tanks differ in no way from those used for the storage of cement, which are described fully in Chapter XIV. Such a stone storage will consist of a row of two or more concrete silos. These are usually supported from 8 to 15 feet from the ground on a deck slab and piers in order to allow the drawing out of the material on to a system of belt or bucket conveyors. The stone is usually fed out of the bins by means of automatic feeders such as are described for use with stone dryers. Among those mills which employ a stone storage of the silo type are the El Paso Portland Cement Company, El Paso, Tex., and the Giant Portland Cement Company, Egypt, Pa.

A good construction for the rectangular storage is concrete and steel. The walls of the store-house should be of concrete and these may be either made thick with a slight taper from the bottom or thinner and buttressed sufficiently to stand the pressure of the stone. The roof trusses may be made to rest directly on the bin walls while the belt conveyors for bringing in the stone are carried in the trusses.

Whether the bins are of steel, concrete or wood the materials are usually drawn out of them by means of a tunnel running under them. The bottom of the bin should have openings controlled by slides at frequent intervals and spouts should lead from

these on to a belt conveyor in the tunnel. Figs. 14 and 15 show good arrangements for a stone-storage house. The walls are of concrete and the roof trusses of steel.

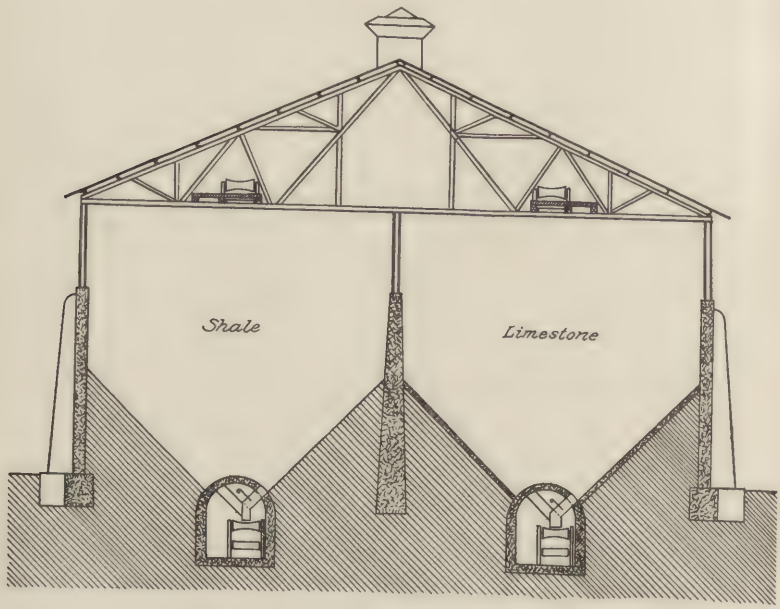


Fig. 14.—Good form of raw material storage.

At the plant of the Edison Portland Cement Company the walls of the stone-storage are formed of sloping triangular-shaped banks of earth on which the roof trusses rest. The outer slopes are turfed and serve to drain off the water while the inner ones, which are lined roughly with stones between which no mortar is used, serve to form a hopper-bottomed bin. The cement-rock is drawn out by means of spouts and belt conveyors running in a tunnel.

Another excellent storage is one consisting of several long rectangular and fairly deep reinforced concrete bins filled by means of an overhead belt conveyor. This latter is in turn equipped with a traveling tripper (see Fig. 15). This tripper is so

designed as to move slowly at a regular rate back and forth over the entire length of the bin and spread the material in uniform layers over this. If the bin is relatively narrow and the openings below are alternately to each side of the center line, the segrega-

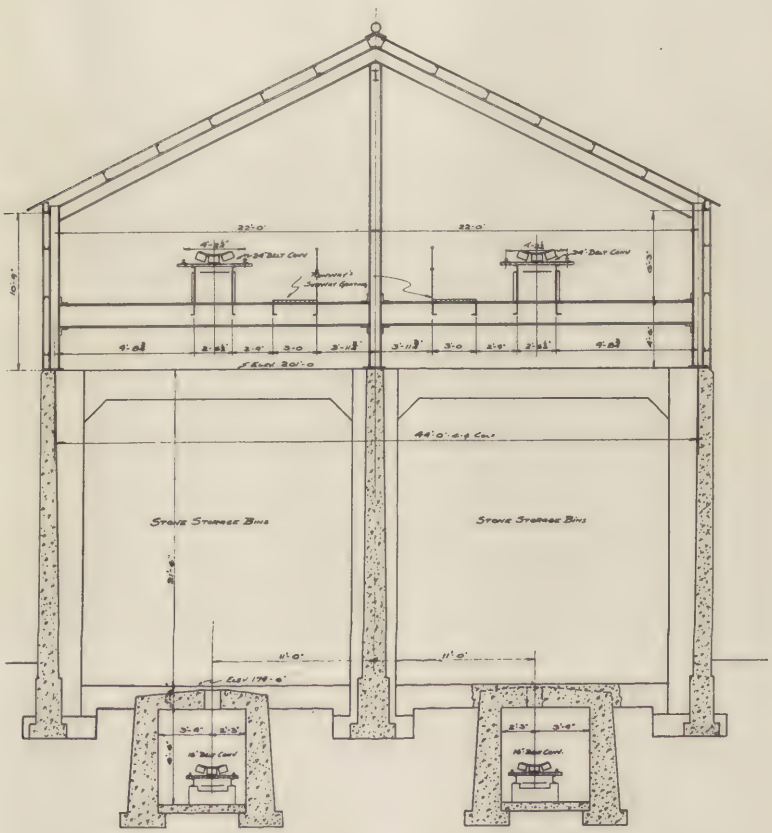


Fig. 15.—Reinforced concrete stone storage.—National Cement Co., Montreal, Can.

tion between coarse and fine material is negligible where the stone is drawn from several openings.

For those who prefer a pan conveyor or bucket carrier to the belt conveyor, the buckets can be arranged to deposit the

material at a number of points in the bin. No doubt, other methods of securing the same result are available. Where a silo-storage is employed, if the number of bins is sufficient to permit it, better results will be obtained by filling or emptying a number of these at the same time by some such method as I have suggested, rather than to fill and empty in rotation.

Many of the newer plants are employing for crushed stone storage a traveling crane and grab bucket. This consists (see Chapter XIV) of a bridge or beam on which a trolley or bucket carrier operates and a heavy clam shell bucket. The bridge in turn travels on two rails which are supported either by two parallel concrete walls or on two parallel rows of steel columns. Where bin storage is employed the walls of the bin carry the tracks for the bridge and the roof. The latter is advisable in a dry process plant in any latitude, but in a wet process plant may be dispensed with for limestone storage where snow and ice will not cause the rock pile to freeze up. The clay storage should of course have a roof.

The walls of the bin must be designed to stand pressure and if desired the storage may be cut into various compartments to separate different grades of rock by means of concrete cross-partition walls, etc. It will be found cheaper where this will answer to employ a steel frame to carry the crane and roof rather than the concrete walls. A combination of an 8-foot or 10-foot concrete wall, with steel columns resting on this is also a good arrangement.

This form of storage is satisfactory both as regards the efficiency with which the materials can be handled and for supplying the mill with rock of uniform composition. With this outfit the material as crushed can be uniformly distributed over a large pile. There is no segregation of fines and coarse and the reclaiming can also be distributed over a large area. It is a simple matter for the chemist to work out for the crane operator a cycle for filling and emptying such a storage which will give uniform material and leave nothing to the judgment of the operator. When such a storage is used the crushed material is usually dumped into one end or at the side of this by means of an eleva-

tor or an inclined belt conveyor leading from the crusher, the crane distributing the stone in the bin.

Sometimes (as where the clay is handled in a wash mill) the storage can be so arranged that the crane can drop the reclaimed limestone into the bins above the grinding mills and the clay into the wash mill, and so save elevators. The most usual arrangement, however, is for the crane to drop the materials into small bins or hoppers located above the weighing device used for proportioning the two.

The stone storage should in most cases hold enough of both materials to keep the mill running for at least a week without necessitating shoveling the rock from that portion of the bins not emptied by gravity or reached by the grab bucket.

Weighing the Raw Materials

In some instances the weighing from bins is done by means of hopper scales. These of course require the constant care of an attendant who controls the filling and emptying of the scale hopper by means of a door in the bottom of the latter and slides on the bottom of the clay and limestone bins. Usually these materials are not run directly into the scale hopper from the large storage bins but first conveyed into smaller bins located above the scale hopper, and from these bins the material flows into the hopper by means of a spout and is stopped at will by a slide or gate. These hopper scales are usually provided with two beams one for limestone and one for shale or clay. These scales are fixed so that the beams may be locked in a box and only the pointers appear. The chemist sets the poise on each beam with the weight of that material desired and locks the case so that the weight can not be altered. As the limestone or shale is run into the hopper the operator turns the key of the beam assigned to which ever is being weighed and continues to run in the material until the beam balances, when the flow of material is stopped by means of the gate or slide. Sometimes this is done automatically by means of an electrical device attached to the beam. One material is of course added after the other.

Automatic scales are now coming into use at the newer plants for weighing the two components of the mix. In each case a pair of these scales is employed, one for each material, and the two scales are so fixed that no matter which fills first they will dump simultaneously. All forms of these automatic scales are delicate

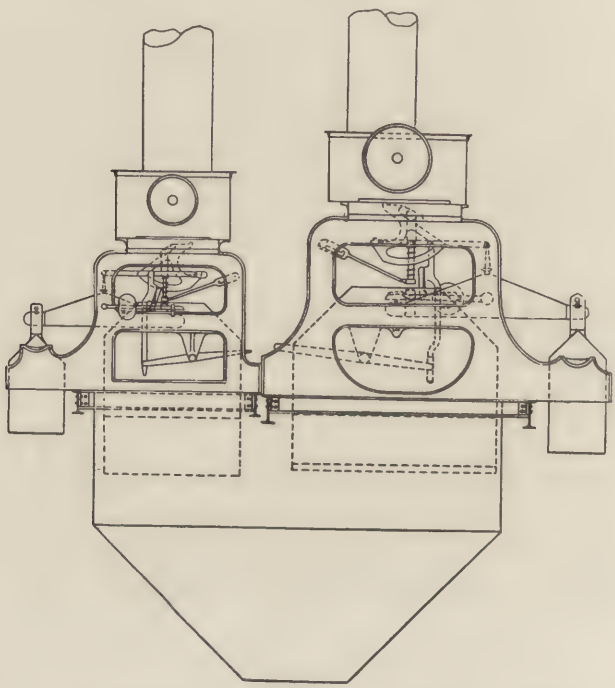


Fig. 16.—Avery tandem automatic scales for raw materials.

and somewhat liable to get out of order but they do away with manual labor and hence lower manufacturing costs.

Fig. 16 shows a pair of Avery tandem automatic scales. These scales are used at the plant of the Tidewater Portland Cement Co., not only for weighing the raw materials but also for weighing clinker, cement, coal, etc. Other makes of automatic scales employed in cement plants, are the Richardson scales and those of the Automatic Weighing Machine Co.

Sometimes scales are mounted on a movable carriage so that they can be shifted under any one of a series of bins, but usually they are fixed in one place and the material brought to them by means of a screw conveyor. This may discharge directly into the scale or else into a small bin above the scale. If the former plan is followed, the conveyor should be continued beyond the scale, so that the material not taken by the scale (as happens when the scale dumps) can be dropped into a suitable elevating and conveying device to be carried back into the bin from which it came.

Scales not only serve to accurately mix two materials but also to keep account of the total quantity of stone, etc. employed. They should be frequently checked as to the accuracy of the weight and watched to see that they dump together.

The Schaffer Poidometer is now much used for proportioning the raw materials in cement manufacture (see Fig. 17). This

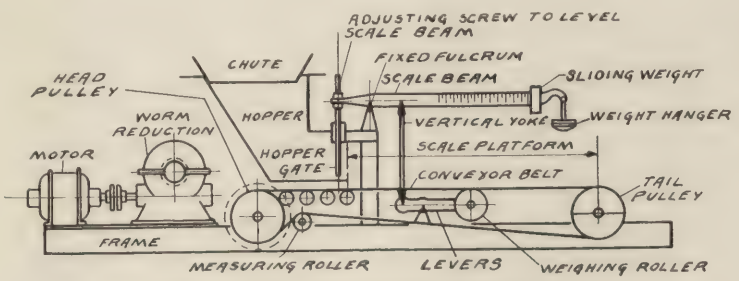


Fig. 17.—Poidometer.—Schaffer Poidometer Co.

consists of a belt supported beneath a hopper by means of a series of fixed rollers. Following these latter and also supporting the belt is a roller which is suspended from a lever arm which in turn controls the opening by means of which the material flows from the hopper on to the belt. When the material runs from the hopper on to the belt, the latter will sag from its weight. The roller under the belt receives this weight and in turn pulls on the walking beam proportionately to the weight which it receives. This pull is offset by a weight which may be set in any desired position. When the flow of material is too great the roller falls cutting off the flow of material to the belt, etc. The poidometer

is adjusted by means of the weight on the beam and may be made to feed material sufficiently evenly and accurately to answer the requirements of the cement mill. Two poidometers are employed, one for limestone and one for shale (or clay) and these are set to give the desired amounts of material.

The scales usually dump or feed simultaneously into a hopper, which in turn discharges on to a belt conveyor. This latter carries the material to the driers or to the bins above the grinding mills. Sometimes, but not often, a mechanical mixer is placed below the scales. This usually consists, when used for mixing crushed material, of drums fitted with flights similar in appearance and action to concrete mixers, or when employed for mixing partly ground materials of a cut flight conveyor. Usually, however, the driers and grinders are depended on for the mixing.

CHAPTER VII

THE DRY PROCESS

Outline of the Dry Process

Figure 18 shows in diagramatic form the steps of the dry process of cement manufacture. The methods employed for

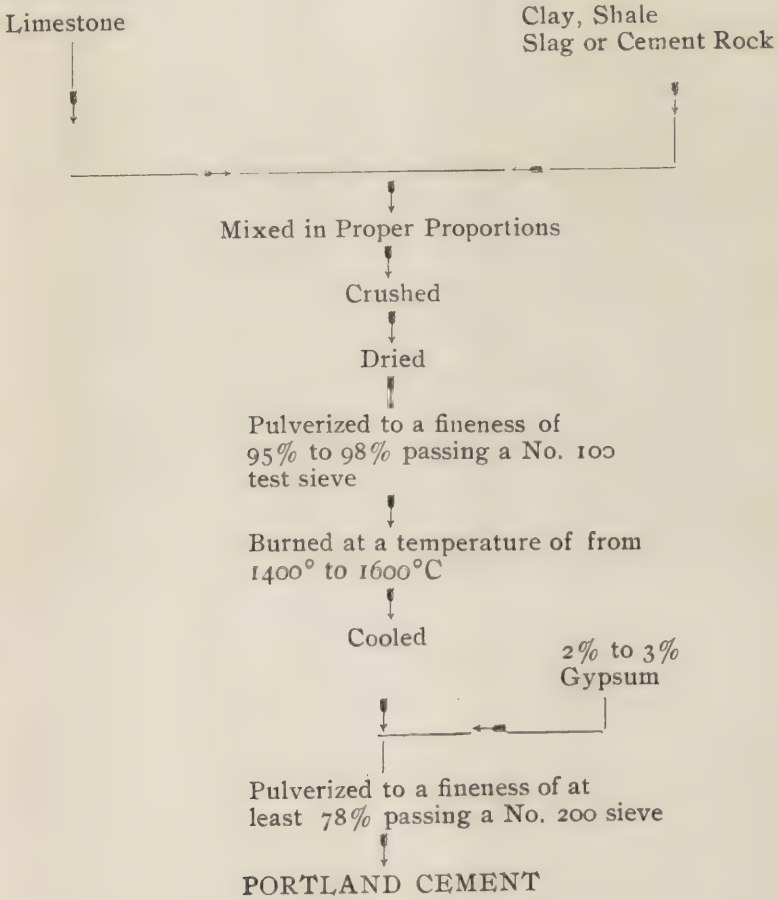


Fig. 18.—Diagram showing steps in the manufacture of Portland cement by the dry process.

mixing and storing the raw materials have been described in the preceeding chapter, while the various crushers and pulverizers commonly employed in both processes are described in detail in the next. The purpose of this chapter is, therefore, to present in sequence the various steps of the dry process up to the burning.

As has been previously stated, the raw materials may be mixed either before or after the primary crushing. The drying always follows the crushing but sometimes the mixing of the two materials may be deferred until after the material is coarsely ground and just before final pulverization in the tube mills.

We thus have four alternative schemes. (1) To crush, dry, pulverize, etc., the two materials together. (2) To crush separately and then mix, dry, pulverize, etc., together. (3) To crush and dry separately, mix and then pulverize the mixture. (4) To crush, dry and partially pulverize the two materials separately, mix and then finely pulverize the mixture, etc.

The first method is entirely satisfactory where the raw materials are two grades of cement-rock, or are cement-rock and limestone. The second and third methods are generally employed when limestone and shale are used and the third and fourth methods when clay is to be mixed with limestone.

The merits and demerits of these various schemes from a chemical standpoint have been quite fully discussed in the preceeding section. From a mechanical standpoint, there is much in favor of mixing at as early a stage in the process as is possible, as this evidently diminishes both the apparatus required and the attention necessary. When the two materials are kept separate, each must have its own crushing plant, storing bins, dryers, conveying system, etc.

Crushing and pulverizing may, of course, be considered as two stages in the reduction of the material from the size brought to the mill to the fine powder necessary for burning. In modern cement mills, this reduction takes place in from three to five steps (depending on the apparatus employed), of which we usually speak of the first two or three as crushing and the last one or two as pulverizing. Drying is merely incident to grinding, as it is not practicable to grind damp or slightly moist materials. The drying

takes place after the crushing and not before, because, obviously, it is easier to handle crushed material in the dryer. Indeed if it were practicable to do so, there would be an advantage in drying the rock before crushing, since even the crushers handle dry rock more satisfactorily than wet.

By *"crushing"* is generally meant the reduction of the materials from quarry size to pieces the largest of which are from say ½ to 2 inches, while by *"pulverizing"* we mean the reduction of this material from the above size to a fine powder.

The crushing of hard materials is now always done in two stages and sometimes in three. The first or primary crushing may be done in

1. Gyratory or Gates Crushers (Size No. 9 and larger).[1]
2. Jaw or Blake Crushers (36 inches x 24 inches opening and larger).
3. Roll Crushers, Fairmount Crushers (36 inches x 60 inches opening and larger).
4. Hammer Mills (Williams "Jumbo").

The secondary crushing is now done by

1. Hammer Mills.[1]
2. Crushing Rolls.
3. Gyratory Crushers (Size No. 6 and smaller).

Crushing

The work to be done by each crusher will depend upon circumstances. When steam shovels are employed, the primary crushers take the rock as it comes from the quarry and reduce this to a maximum about 6 to 10 inches. The secondary crushers receive the product of the primary crusher and reduce this to a product ranging from ¾ to 2½ inches and under, depending on the type of pulverizers employed. Ball mills and Hercules mills will take limestone crushed to 2½ inches, but Conpeb, Griffin, Fuller, Kent and Sturtevant mills require a somewhat finer feed.

The primary and secondary crushers should be so balanced as to handle the rock most efficiently. Sometimes where the primary crushing is only to 10 inches, as is the case with very large crushers, and the type pulverizer employed requires a rock

[1] All of these machines are described in the next chapter.

crushed quite small, the secondary crushing is done in two steps —usually two hammer mills being employed. At most cement plants, however, two-stage crushing is all that is necessary.

At a few small plants or plants built fifteen or twenty years ago, the crushing is done in one stage; one or more gyratory crushers (No. 5 to No. 7½) being employed, but this practice is now obsolete in America. In the early days, it was quite common to install No. 5 or No. 6 gyratory crushers and to follow these directly by a ball mill. The No. 6 crusher may be set so as to crush to 2 inches and under, which is about as coarsely crushed material as the ball mill will handle with any degree of efficiency.

The No. 6 gyratory is about as small a crusher of this type as will crush hand loaded stone, and even with this size crusher, considerable sledging in the quarry is necessary in order to break down the stone to a size which will pass into the opening (12 x 46 inches) of this crusher. On the other hand, gyratory crushers larger than the No. 7½ crusher, which has an opening 15 x 55 inches, can not be set to crush as small as 2 inches. Consequently, when steam shovels were introduced into the cement industry, it was necessary to provide crushers which would handle very large pieces of stone. These large crushers, on the other hand, would not give a product small enough to go to the grinding mills, which made the intermediate crusher necessary.

Gyratory crushers were first employed for the secondary crushing simply because many plants, when they changed from hand loading to steam shovel loading, installed a large gyratory, jaw or roll crusher to do the primary crushing and then sent the product of this to the small (No. 5 or No. 6) gyratory crushers which they formerly used, etc. When new plants were built, however, these generally employed hammer-mills for the secondary crushing.

The most approved crushing plant at the present time is one in which the primary crushing is done by a large gyratory or jaw crusher and the secondary crushing by a hammer-mill. When the stone is soft, as in the case of cement-rock, a roll jaw crusher of the Fairmount type also gives excellent results for

primary crushing. The gyratory crusher should not be smaller than No. 18 and the jaw crusher should be at least 36 x 42 inches, if steam shovels are employed in the quarry.

The product of the first crusher should preferably be fed by gravity into the secondary one. This, of course, necessitates setting the primary crusher high up on massive concrete piers. When this is undesirable, a large bucket elevator or an inclined belt conveyor may be employed to take the stone from this crusher to the smaller ones. In some instances, the primary crusher is located at the quarry and the secondary ones at the mill. At others, both the primary and secondary crushing is done at the quarry. In either case, the rock is conveyed to the mill in cars, by aerial tramway, or by a long belt conveyor.

The hammer mill should be capable of taking the product of the primary crusher and delivering this in a proper condition for the pulverizers. The hammer mill should also have sufficient capacity to take practically the full quantity of material the primary crusher delivers to it. In other words, no intermediate storage should be required, although it is advisable to discharge the primary crusher into a pocket or hopper of a few cubic yards capacity and to feed from this to the hammer mill by means of a pan conveyor or a belt conveyor, the latter acting as a feeder. This arrangement prevents choking the hammer mill, should a car of fine material be sent from the quarry. Material in such condition would need but little crushing and consequently might pass through the primary crusher in such volume that the hammer mill could not handle it. This is particularly true when jaw and roll crushers are employed ahead of the hammer mill.

Sometimes the product of the primary crusher is passed through a rotary screen in order to separate from it any fully crushed material and allow only the big pieces to go to the secondary crusher. While this relieves the latter of some work, the screen has to be revolved and the extra handling of the stone represents a source of trouble which more than balances the gain at the secondary crusher, so that in general it will be found more satisfactory to pass all the stone directly from the primary to to the secondary crusher.

Fig. 19.—Crushers—Tidewater Portland Cement Co. (One No. 9 and two No. 6 gyratory crushers).

At a few plants, the quarry cars are dumped into some form of feeder which feeds the stone into the crusher at a uniform rate. These consist of slow moving heavy pan or apron conveyors, reciprocating feeders such as are described under Dryers or slow moving parallel chains. The general practice, however, is to dump the contents of the quarry cars directly into the crusher, a metal hopper or chute being built above the crusher to receive the stone.

The machines are massive and repairs generally require handling large parts. It is well, therefore, to install a crane on a bridge beam moving over both crushers in order to handle the repair parts, etc.

There should be a hook fastened to an iron cable and pulled by an air hoist installed above the crusher so that large pieces of

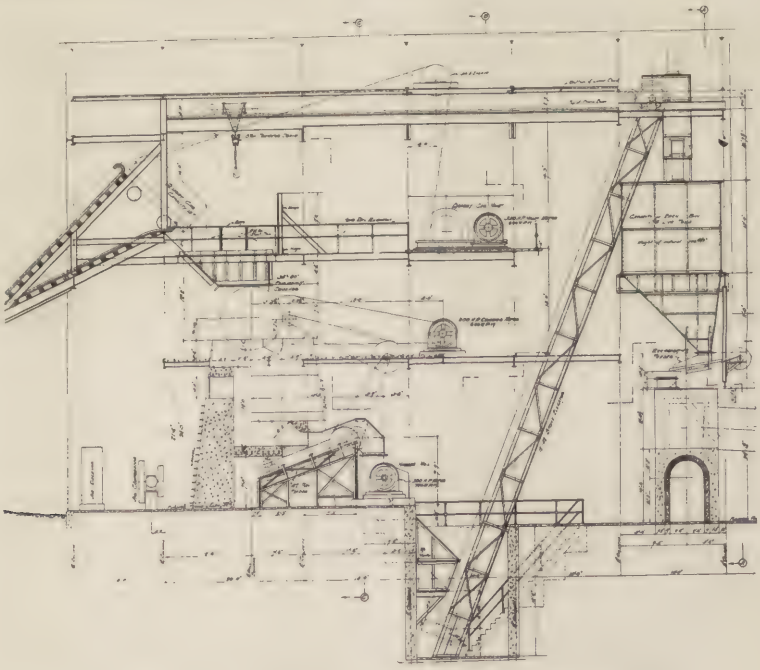


Fig. 20.—Crushing Plant—National Cement Co., Montreal, Que., Richard K. Meade & Co., Engineers.

stone which become wedged in the latter may be lifted out or turned around so as to go in.

Figures 19 and 20 show two crushing plants. In each instance the equipment is evident from the drawing.

Drying and Dryers

The dryers used for drying all cement raw materials may be classed under two heads—direct fired dryers and waste heat dryers. The former are heated by means of a fire box at one end of the dryer or by an oil or powdered coal jet and the latter by the hot waste gases from the rotary kilns. With both forms the rock is fed in at the upper end and works its way out at the lower.

Direct fired dryers (Fig. 21) are cylindrical in shape, from 5 to 8 feet in diameter and from 50 to 80 feet in length. They are similar in construction to the rotary kiln described in Chapter XI. The form shown is heated by means of coal fired on grates in the fire box shown at the discharge end. The cylinder is inclined from the horizontal at a pitch of from ½ to ¾ inch to the foot and is usually provided with angle or channel irons bolted to the inside to act as shelves to carry the rock up and expose it to the hot gases. (See Fig. 22). Some dryers have their upper half divided into four compartments by means of plates in order to expose a greater surface of rock. (See Fig. 23). Until recently direct fired dryers were usually fired by means of hand stoking on grates. Now pulverized coal is much used. This not only saves labor but also increases the capacity of the dryer over hand firing.

The temperature of a dryer is kept too low to admit of proper combustion of powdered coal in the dryer itself and this is usually secured by employing a fire box or combustion chamber at the end of the dryer.

When it is desired to change a grate or stoker fired dryer to pulverized coal the installation is simple and nothing is necessary except to tear out the grate bars and protect the end of the dryer from burning out by a proper shield of fire brick, if this does not already exist. The fire-doors are then removed and the

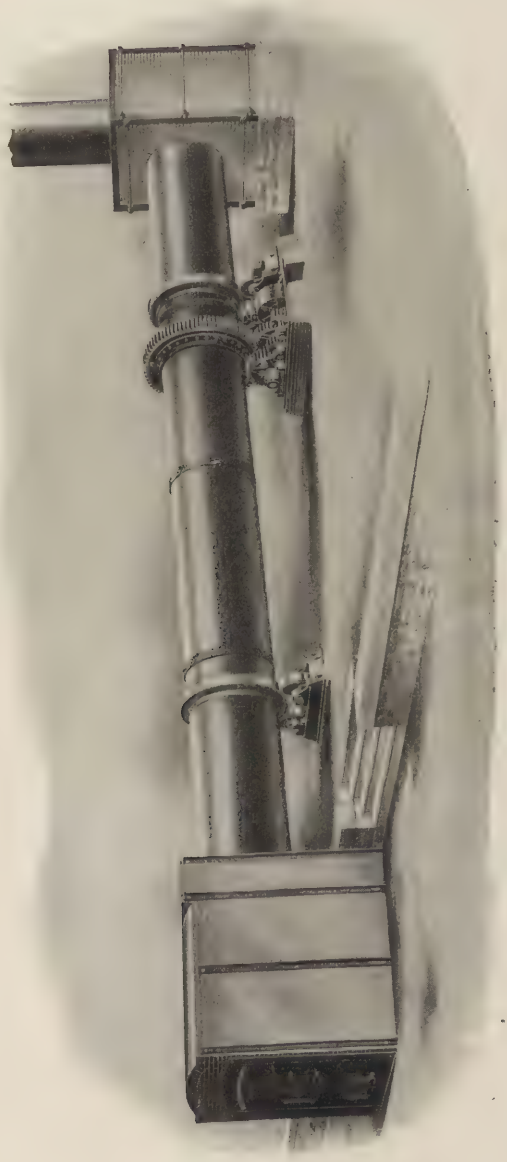


Fig. 21.—Rotary direct fired dryer.

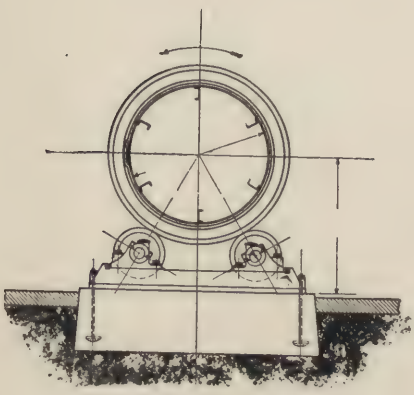


Fig. 22.—Rotary dryer shelver.

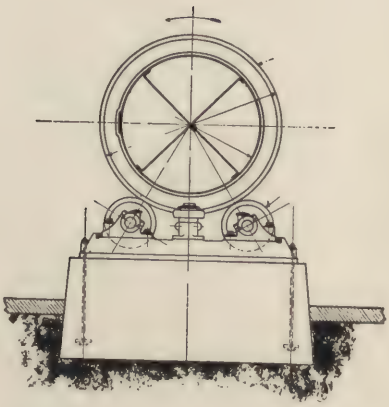


Fig. 23.—Rotary dryer compartments.

burners inserted in their place, the space around being stopped up with fire brick. If the furnace is small, it may be necessary to make a few openings in the side to protect the walls from scorifying, etc. Fig. 24 shows the installation of powdered coal in an old grate setting.

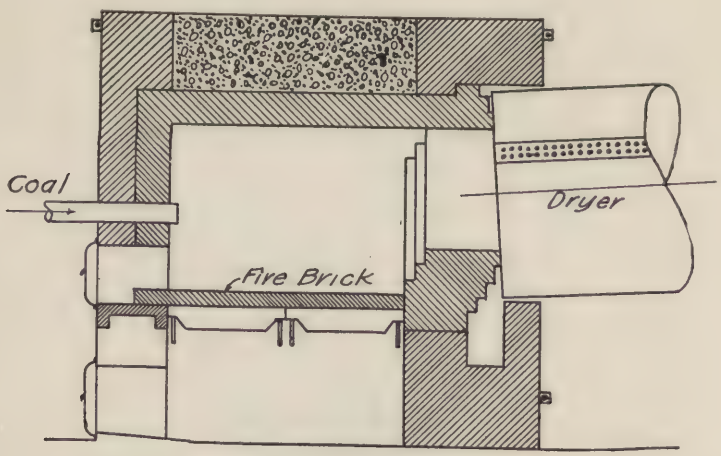


Fig. 24.—Method of installing pulverized coal firing in case of dryer previously fired by hand.

With dryers a slow, lazy flame is desired; hence only a small amount of air is allowed to enter with the coal and the balance is drawn in through openings in the front and sides of the furnace.

When a new dryer is to be installed, a combustion chamber of special design may be employed, and such a combustion chamber will be somewhat cheaper than the ordinary dryer fire box. Fig. 25 gives the details of such a combustion chamber suitable for a 6 x 50 foot rotary dryer. Modification of this de-

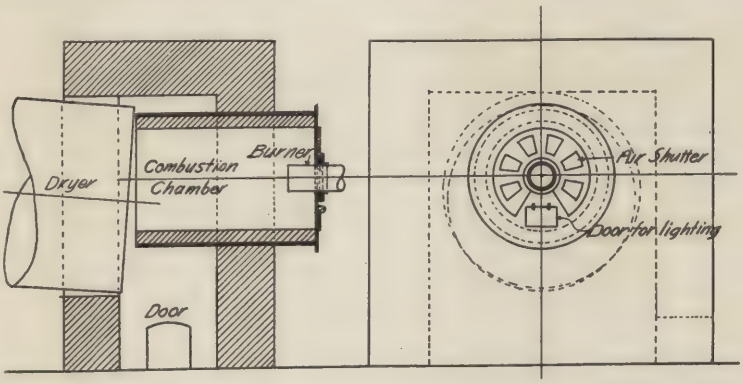


Fig. 25.—Combustion chamber for heating dryer with pulverized coal—Meade system.

sign to suit various other sizes can easily be made by allowing about the same proportion between the combustion space and the dryer.

Capacity of Rotary Dryers

The capacity of an ordinary rotary dryer, where the length is about ten times the diameter, is about 125 pounds (in the case of clay) to 150 pounds (in the case of hard limestone) of water evaporated per square foot of cross-section per hour. The area of cross-section of a 5-foot diameter dryer, for example, is 19.6 square feet. If this dryer is 50 feet long its capacity on limestone is therefore 2,940 pounds of water per hour. If the limestone to be dried contains say 5 per cent moisture, there would have to be evaporated 105 pounds of water per ton of material dried and the capacity of the dryer would be 28 tons of dried material per hour.

TABLE XIII.—Capacities of and Power Required to Operate Direct Fired Rotary Dryers

Material	Limestone		Shale			Clay			Size of motor required to operate	Speed of rotation
Moisture in wet material	3%	5%	5%	8%	10%	15%	20%	25%		
Pounds of water to be removed per ton of material dried	62	105	105	175	223	352	500	666		
Approximate coal required per ton of material dried in lbs.	11	18	19	32	50	70	100	133	R. P. M.	H. P.
Size of dryer Diam. Length	Capacities in tons (2,000 lbs.) of dried material per hour									
4 ft. × 40 ft.	30	18	16	10	6½	4½	3	2¼	7½	4
5 ft. × 50 ft.	47	28	26	15	10	7	4½	3½	10	3
6 ft. × 60 ft.	67	42	38	22	14	10	6¾	5	15	2
7 ft. × 70 ft.	92	55	52	30	20	13	9	7	15	1¾
8 ft. × 80 ft.	120	72	67	40	26	18	12	9½	20	1½

The fuel requirements are about 1 pound of coal for every 5 or 6 pounds of water. The above dryer would, therefore, require about 490 pounds of coal per hour based on the higher ratio.

Table XIII gives the capacities of various sizes of dryers on material of varying percentages of moisture, power to operate, etc.

Waste Heat Dryers

The waste heat dryers were the invention of the late Mr. Charles A. Matcham, of Allentown, Pa. These dryers are similar in every respect to the ordinary direct fired dryer described above except that they are made somewhat larger and have no fire box. The arrangement with reference to the kiln is shown in Fig. 26. The dryers, as will be seen from this, are immediately back of

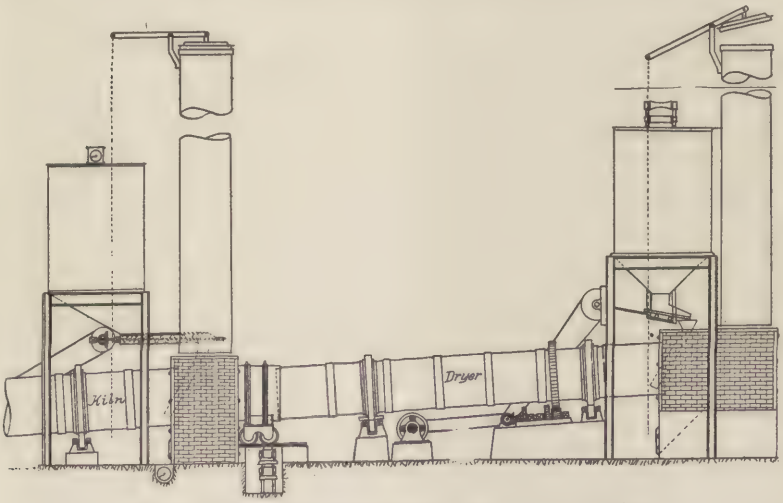


Fig. 26.—Dryer arranged to utilize waste heat from kilns.

and in a line with the kilns, so that they can receive the waste gases of the latter with as little impediment to the draft as possible. Between the dryers and kilns is the customary dust-chamber (see Chapter XI) and on this rests a stack provided with a damper. When the dryers are in use, this damper is closed and the kiln stack is not used, all the gases from the kiln

passing through the dryer. As the gases from a 125-foot rotary kiln are at about 900-1,600° F. and there are at least 250,000 B. t. u. (18 pounds of coal) in the gases entering the dryer per minute no difficulty is experienced in drying large quantities of material very thoroughly by means of these waste heat dryers. There is usually a movable housing between the dryers and dust-chamber to allow easy access to the former for repairs without shutting down the kiln. The stone from the dryer drops down through an opening in the housing into a pit, from which it is elevated to the storage or stock-bins by means of bucket elevators. In order not to effect the capacity of the kilns, these dryers must be of large diameter and must be provided with taller stacks than are ordinarily employed for kilns or direct fired dryers.

These waste heat dryers save the coal used in heating the ordinary direct fired dryers and also the labor necessary to stoke them. This saving in the cost of manufacture approaches one to two cents per barrel, depending upon the moisture in the raw materials and the cost of coal. The waste heat dryers also dry very thoroughly, and sometimes even break down the structure of the rock, due to the high temperature of the gases passing through them, thus often effecting a saving in the cost of pulverizing.

It is doubtful if waste heat dryers will be employed to any extent in the cement industry in this country in the future except where power can be purchased cheaply, as the waste heat boiler offers a much more efficient method of utilizating the heat in the gases. The number of B. t. u. required for drying the raw materials at most dry process plants does not exceed 35,000 B. t. u. per barrel, whereas the requirements for steam raising with turbo-generators are say 310,000 B. t. u. per barrel of cement. Since the waste gases from burning one barrel of clinker contain between 400,000 and 500,000 B. t. u., the employment of waste heat dryers in place of boilers entails a loss of at least 365,000 B. t. u. per barrel. In a plant of 3,000 barrels per day output, this amounts to about 40 tons of coal per day. It will be seen, therefore, that it pays better to employ direct heat dryers and waste heat boilers rather than to reverse the process.

Drying Clay

Sometimes in drying clay, this latter balls up in the dryer. The outside of these clay balls bake hard but the inside, even after they have passed through the hottest part of the dryer, remains wet. In drying such clays, therefore, it is found most successful to do the drying in two stages, first passing the clay through a dryer, then through a set of rolls or other disintegrator to break open these balls and allow the heat to get at the moisture remaining in the center of the lumps and then through a second dryer in which the remaining moisture is driven off. The clays along the Hudson river used by the Alsen and other plants there are very plastic and ball up and bake in this way. Here this system of drying has proved very efficient.

Clays often contain considerable moisture and when this is the case much coal is necessary to dry them, hence waste heat dryers will here often effect a great saving over direct fired dryers. Slag which has been granulated by water, as is always done when this material is used for Portland cement, is particularly hard to dry and the expense of drying granulated slag, often carrying as much as 20 per cent water, almost balances the fact that it is a waste product and may be obtained for nothing by the companies using it.

Feeding the Dryer

Dryers are sometimes fed directly from the stone storage and sometimes from the secondary crusher, in which case the dryer must take the stone as rapidly as it is fed from storage or as delivered by the crusher. A more approved method is to install a bin above the feed end of the dryer and to feed the material to be dried out of this at a regular and uniform rate suited to the capacity of the dryer and the moisture in the material. For feeding the material, a reciprocating table feeder is generally used. This consists simply of a table placed at a slight inclination from the horizontal. This table is moved backwards and forwards beneath the opening at the bottom of the bin by means of an arm and an eccentric, the material spilling over the end at each backward stroke. The amount of rock fed may be adjusted

by either a slide in front of the opening or by varying the length of the stroke, which can be adjusted at the eccentric.

Pulverizing the Raw Materials

The final reduction of the raw material to the proper fineness for burning is usually effected in two stages, by one of the following ways:

1. Hercules Mills followed by Tube Mills.
2. Ball Mills followed by Tube Mills.
3. Kominuters followed by Tube Mills.
4. Griffin Mills followed by Tube Mills.
5. Kent Mills, Screen Separators and Tube Mills.
6. Sturtevant Mills, Screen Separators and Tube Mills.

Or in one stage by one of the following mills:

7. Compeb Mills.
8. Griffin Mills.
9. Fuller Mills.
10. Sturtevant Mills and Air or Screen Separators.
11. Kent Mills and Air or Screen Separators.
12. Raymond Mills.

Most of the newer dry process plants are equipped with Hercules mills and Tube mills. The older plants quite generally employ tube mills using either ball mills, Kominuters or Griffin mills to prepare for these. Griffin mills and Fuller mills are still used to some extent, while a few plants employ Sturtevant or Kent mills, either for full reduction or for preparing for the tube mill.

Degree of Fineness of the Raw Materials

Three variables enter into the production of Portland cement clinker, *viz:*—temperature of burning, length of time in the kiln and the fineness to which the raw materials have been reduced. This may be expressed mathematically as an equation thus: $A \times B \times C = D$, in which A represents time; B, temperature; C, fineness, and D, a constant namely, clinker. If we increase any one of the three variables A, B and C, it will decrease one or both of the other two. Thus by increasing the time in the kiln,

we decrease the temperature necessary to clinker, while if we grind the materials more finely we decrease either the temperature or the length of time in the kiln and may thus increase the output of the kiln and decrease the fuel required per barrel.

In Portland cement clinker, no actual fusion has taken place, merely sintering or diffusion between the elements of the limestone and clay. That is, the silica and alumina in the clay particles diffuse into the lime of the limestone and vice versa. The rate or rapidity of diffusion as well as the temperature at which it takes place depend upon the surface exposed. This is a general law applicable to all solids and solutions, therefore, the finer the raw materials are ground, the greater area of surface is presented and consequently the greater chance for diffusion.

The actual degree of fineness to which the raw material should be ground depends largely upon conditions. It may be said, as a general rule, that it should never be ground coarser than 90 per cent through a 100-mesh sieve and that in most cases 95 per cent to 98 per cent is required to produce a sound cement. The fineness of the raw material should be tested at least once a day and, if possible, two or three times a day in order to have a check upon the work of the mills and to keep them up to standard. The raw material can be tested on the 100-mesh sieve by the method for fineness outlined in the section on "Physical Testing."

In general, it may be said that most of the trouble experienced in making a satisfactory product by cement mills is due to improper grinding of the raw materials. Fine grinding of the raw materials will always pay as it reduces not only the coal required for burning but also increases the output of the kilns and results in a greatly improved product.

Elevating and Conveying Machinery

The raw materials are carried from one stage in the process to the next by means of mechanical conveyors. The product of the large gyratory crushers is difficult to handle and where this must be conveyed, belt conveyors may be employed to advantage. Probably the best method of elevating where space permits this is an inclined belt conveyor. Where this can not be used, con-

tinuous steel bucket elevators employing buckets of very heavy construction and roller chain are often employed. The service on such elevators is very severe and they must be very substantially made. Belt elevators of this type are not satisfactory and in fact belt elevators are seldom used in cement plants. The size of the bucket depends entirely on the size of the stone to be handled and on the quantity of this. The elevators are, of course, very slow moving and are driven by a pair of toothed sprockets at the head end. These large elevators should be provided with some automatic brake so that if the motor driving them stops they will not reverse from the load in the buckets and dump the material in the boot of the elevator, making it necessary to clean the latter out before the elevator can be started again.

The product of small gyratory crushers and hammer mills can be handled in any of the ways mentioned above. Owing to the size of the material, smaller and less rugged buckets may be employed. The stone may also be conveyed horizontally by means of a drag chain with large links.

The product of the ball mills, the Hercules mills and other granulators can be conveyed laterally by means of screw conveyors or belt conveyors. The former are probably more generally employed. Ordinary malleable iron single or double strand bucket elevators are generally used for elevating material of this type.

The product of the tube mills and the finely ground raw material ready for the kiln can be handled to advantage by any of the methods described in the preceeding paragraph.

The Fuller-Kinyon pump has also just come into use for conveying finely ground raw material from the mills to the bins above the kilns. This pump is fully described in the section on Pulverized Coal, to which the reader is referred.

In the older mills elevators and conveyors were usually driven by means of chain or belt drives and this generally made a countershaft necessary even when individual motor drives were used. Elevators and conveyors are now often driven directly from a

motor without belts or chains by means of some form of worm or spur-gear speed reducer. The spur-gear reducers of the Jones type were first employed for unit drives but in many of the newer mills worm-gear reducers such as the Hindley, Cleveland or De Laval are employed. The worm-gear reducers save room and therefore economize building space. In the case of either type of speed reducer, the motor is attached to the shaft of the worm by a flexible coupling, and the head shaft of the elevator or conveyor to the shaft of the gear by the same means. Back-geared motors are also used to some extent to drive elevators and conveyors, but the reduction of speed in the motor itself is seldom enough to allow them to be used without a counter-shaft or speed reducer.

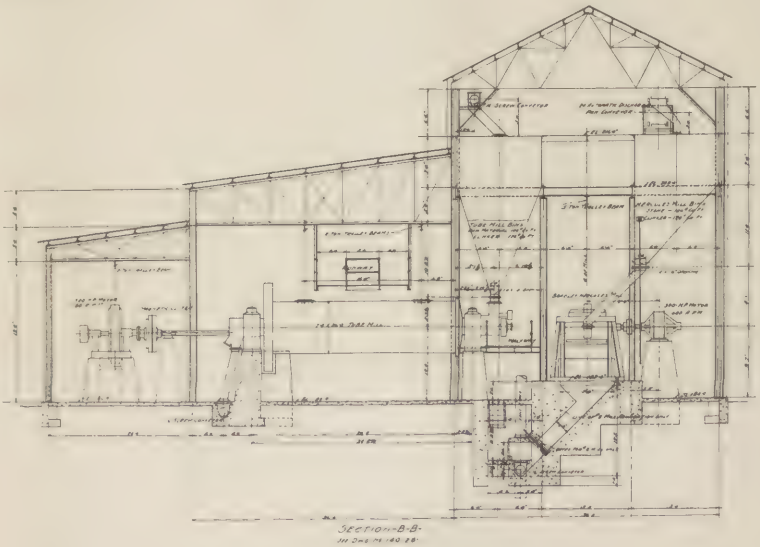


Fig. 27.—Raw mill—National Cement Co., Montreal, Que., Richard K. Meade & Co., Engineers.

Complete Raw Mill

Fig. 27 shows a section of the complete raw mill of a modern dry process cement plant. As will be noted this is equipped with Bradley Hercules mills and 7 x 26 foot tube mills. The ar-

rangement is evident from the drawing. In this particular plant, there are four units all arranged as shown in one room. Two units are designed for grinding the raw materials and two for grinding the clinker, but by an extension of the conveying systems the mills are so placed that any mill can be used for grinding cement and any mill for raw materials.

CHAPTER VIII

THE WET PROCESS

History of The Wet Process

The first materials used in Europe were the soft chalks of England. These carried considerable water as excavated, and in the old shaft kiln process of burning[1] it was also necessary to mold the material into bricks. The general method of operation, therefore, was to grind the two materials together in a thick "slurry" and allow this to settle, drain the water off, and break up the resulting mass into blocks, which were dried and fed into the kiln.

In northern Germany, these same soft chalks of the North Sea coast were used, and the process was quite similar to that employed in England. When plants were started in Southern Germany, these used hard materials, but, as the molding into bricks was necessary, the plants here naturally followed the method of those in the north.

In America, the first successful plant employed the cement-rock of the Lehigh district. This was a solid and compact material, carrying only a very small quantity of moisture. Saylor and his co-workers knew nothing of foreign practice, except what they had been told, so they followed their own ideas, which consisted in grinding the rock dry and only incorporating with it sufficient water to mold it into the blocks necessary for charging the vertical kiln. When the rotary kiln was introduced here, this material was still ground dry, but in the very early stages of the process, a small amount of water was added to it just before it was fed into the rotary kiln, under the belief that it would perhaps otherwise be blown away. The addition of water, however, was soon discontinued and all the subsequent cement plants of the Lehigh district employed a straight dry process.

[1] See page 244 et seq.

As rotary kiln plants were built in other parts of the country, when they employed dry materials, they followed quite closely the practice in the Lehigh district.

The wet process plants in this country were, in the early days of the industry, confined exclusively to the manufacture of cement from marl and clay. This material, carrying as it did approximately 50 per cent to 60 per cent of water, was manifestly not adapted to drying before grinding, and very properly the manufacturers who were using it believed that the drying operation could be most successfully carried out in the rotary kiln itself.

With the introduction of the manufacture of cement in the West, difficulties were encountered in certain plants. What these difficulties were need not be gone into extensively here, but it is sufficient to say that they were connected with the quality of the product and occurred in a section where fuel (natural gas) was very cheap. Several of these plants were in charge of German chemists, and one of these believed that the difficulty that occurred with the quality of the product could be overcome by the introduction of the wet process. Working on this theory, the plant was changed to a wet process one, and the alteration did result in improving materially the quality of the product.

This occurrence might have been sufficient to induce all manufacturers who were having trouble with the quality of their product to adopt the wet process, had it not been for the fact that many plants employing similar raw materials were making perfectly satisfactory cement by the dry process and employing less fuel for doing this than were the wet process plants.

Outline of the Wet Process

The wet process of cement manufacture differs from the dry process only in that the materials are ground and burned wet. No drying of the raw materials is necessary. On the other hand, water must be actually added to the raw materials (except in the case of marl and shells dredged from under water and alkali-waste) at some time before they are ground, usually after crushing and just before the raw materials are fed to the pulverizing

machines. Fig. 28 illustrates diagramatically the steps of the wet process where clay is employed as the argillaceous raw material.

When limestone and shale are the raw materials, the wet process does not differ from the dry until the grinding is reached, here water is added, the proportion being from 40 to 60 per cent of the dry raw materials, and the mixture is pulverized. The resulting slurry will contain from 30 to 40 per cent water according to the amount added. It is of about the consistency of a thin mud. Only enough water is used to make the mixture sufficiently fluid to handle easily. Any excess over this is undesirable as it increases the fuel requirements in the kiln. The same machines are used for crushing[1] as in the dry process and a storage[2] for rock is usually provided. The mix[2] may be made at any convenient point, as in the dry process.

When clay is used, the limestone is crushed and handled as in the dry process, but the general practice is to dump the clay into a wash mill and work it up with water into a thin "slip" or slurry, which is fed into the grinding machines at a regular rate along with the limestone. At some plants the clay is mixed in with the limestone as it comes from the pits, either before or after the limestone is crushed.

Marl is usually worked up with sufficient water to make it fluid either in a wash mill, a pug mill or a wet pan; the clay receiving the same treatment in the same apparatus with the marl; or else in a separate machine. In the latter case, the two slurrys are mixed in the required amounts and ground.

Advantages and Disadvantages Claimed for the Wet Process

The following are the advantages[3] claimed for the wet process:

(1) That a better and more uniform cement can be manufactured by the wet process than by the dry, owing to the fact

[1] See pages 175 to 189.

[2] See Chapter VI.

[3] Those who desire to study the relative merits of the two processes will find a discussion of this by the author in *Concrete-Cement Age*, Cement Mill Edition, May, 1921.

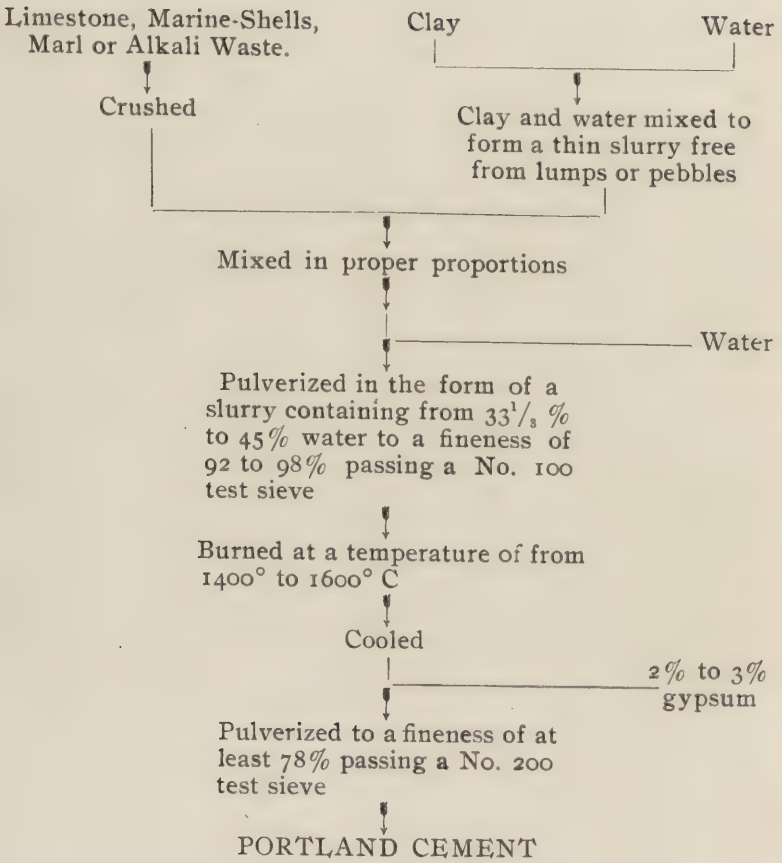


Fig. 28.—Diagram showing steps in the manufacture of Portland cement by the wet process.

that a more satisfactory mixture of the raw material can be made and a more constant composition can be maintained.

(2) That wet materials can be more easily ground than dry, the operation requiring less power and the repair item being less. That the output of the mills is also greater, which decreases the investment in the plant and consequently lessens interest, depreciation, etc.

(3) That the raw materials do not need to be dried which effects a saving of the fuel and equipment necessary for this, with the labor, power, repairs, overhead, depreciation attendant on the latter, etc.

(4) That the clinker of the wet process is more easily ground than that of the dry.

(5) That wet materials are more easily handled than dry.

(6) That there is less dust connected with the wet process than with the dry.

The admitted disadvantages of the wet process are:

(1) That more fuel is required to burn a slurry than is required to burn a dry mixture even when the coal necessary for drying is included.

(2) That greater kiln and fuel grinding capacity is required than in the dry process.

(3) That power is required to agitate and mix the slurry.

For the evidence supporting these various claims the reader is referred to the chapter on burning and to the following paragraphs of this one. The relative fuel requirements of the wet and dry processes and the dust losses of each are quite fully discussed under Burning, while the advantage in chemical control and grinding are discussed below.

Chemical Control of the Wet Process

Chemical control of the wet process is usually secured by some modification of the following system: From the tube mills, the finely ground slurry is emptied into "*correcting basins.*" These are fairly large, usually holding from 3 or 4 hours' run of material. The slurry is continually stirred and consequently is thoroughly mixed and of practically the same composition

throughout the basin. If found not to be of the proper composition, it is possible to add to it a small quantity of clay slip, made by grinding clay and water; or what is more common practice, a succeeding tank of slurry is ground of a slightly higher or lower composition, as the case may require, and the contents of the two basins are then mixed in the proper proportions and run into a still larger basin called the "mixing basin." These latter are often made sufficiently large to hold a full day's run. Their contents also are constantly agitated and thoroughly mixed before being sent to the kilns.

In this way, the contents of the kiln basins are usually of correct and uniform composition. Examination of the records of several wet process plants reveals the fact, however, that in spite of this theoretical opportunity to secure perfect composition, the contents of the kiln basins are often at least 1 per cent and sometimes farther from the composition desired. Even in this process much is left to the skill and good judgment of the chemist. It is also a difficult matter to agitate the large kiln basins thoroughly, and some settling always occurs where the arms of the agitator do not reach.

It will be seen that this system of slurry basins is well adapted to promote proper proportioning of the clay and limestone, but it must be remembered that uniformity of the cement depends very much on the uniformity of the raw materials also. If the cement is to be uniform in its setting and hardening properties there are two ratios which must be kept uniform, namely:

$$\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} \qquad (1)$$

and

$$\frac{SiO_2}{Al_2O_3} \qquad (2)$$

The first of these ratios will determine the soundness, strength, etc., of the cement, but the second will also play an important part in the hardening and setting qualities, and keeping this ratio constant promotes a cement of uniform setting and hardening qualities. The correcting basins will help keep the first ratio con-

stant, but the fixity of the second will depend entirely on the uniformity of the raw materials.

It will be seen at once that in the wet process there are quite a number of steps over and above those required in the dry process, and that some power is also required for stirring the various slurry basins. The quantity of power is appreciable, being about 0.02 horsepower per barrel of cement produced per day, or about 60 horsepower for a 3,000-barrel plant, but it is certainly not sufficient to condemn the operation on the score of power, in view of the excellent opportunity which is afforded to secure uniform composition.

To sum up the arguments as to the quality of the cement produced by the wet process, it appears that it is easier to control the lime-silicate ratio by the wet process, but that this can be done perfectly satisfactorily also by the dry process if the mill is properly arranged for this.

Grinding the Raw Materials

The grinding of the raw materials in the wet process is usually carried out in one of the following combinations:

1. Compeb Mills.[1]
2. Kominuters and Tube Mills.
3. Ball Mills and Tube Mills.
4. Hercules Mills and Tube Mills.

The water is added, if necessary, before the materials are fed into the grinders. If the grinding is in two stages, it is usual to place a small feed bin above the tube mill, in which the partly ground raw material is stored. The contents of this bin are kept continually stirred by means of a paddle agitator.

The argument that wet material can be ground more easily than dry is probably well founded and what data the writer has been able to obtain (largely from metallurgical sources) leads him to believe that a wet tube mill will have greater output than one grinding dry. Most manufacturers are content to take this statement without investigating the actual saving which can be

[1] See Chapter X for description of these mills.

effected by the wet process over the dry, so that actual figures showing the saving of wet over dry grinding in the cement industry are hard to get. It is also probable that while the output of the tube mill is greater with wet grinding than with dry, that the difference between wet and dry grinding in the ball mill is not marked.

So far as the writer's observations go, however, the power equipment installed per barrel of cement produced is fully as large in wet process as in dry process plants.

Generally speaking, about 30 per cent of the total power required to manufacture cement (or about 5 kilowatt-hours per barrel) is employed in the grinding of the raw materials. It will be seen, therefore, that in cement mill practice unless the relative saving in power by wet grinding is very marked, the actual difference between the two processes in the power required for grinding might easily be accounted for elsewhere, such as in the agitation of the slurry, the grinding of the greater amount of coal required for burning, revolving the additional equipment for burning, handling the greater weight of raw material due to water, etc.

Wash Mills

Wash mills are employed to some extent for triturating the clay with water so as to form a homogeneous slurry of the latter. The wash mill is employed because clay being sticky when fed into a crusher with limestone will often choke and gum the latter. It is, therefore, preferable to handle clay and limestone separately. As clay is already in a finely divided condition, no crushing, of course, is necessary and it is ready for the pulverizing machine. A few plants add the clay just as it comes from the clay pit ahead of the grinding machine. It is considered better practice now, however, to work this up into a slurry in a wash mill and then to feed this slurry into the pulverizing mill along with the limestone.

The wash mill, Fig. 29, generally consists of a circular pan or tank made of concrete 10 to 20 feet in diameter, in which revolve a series of harrows or knives, which break up the clay

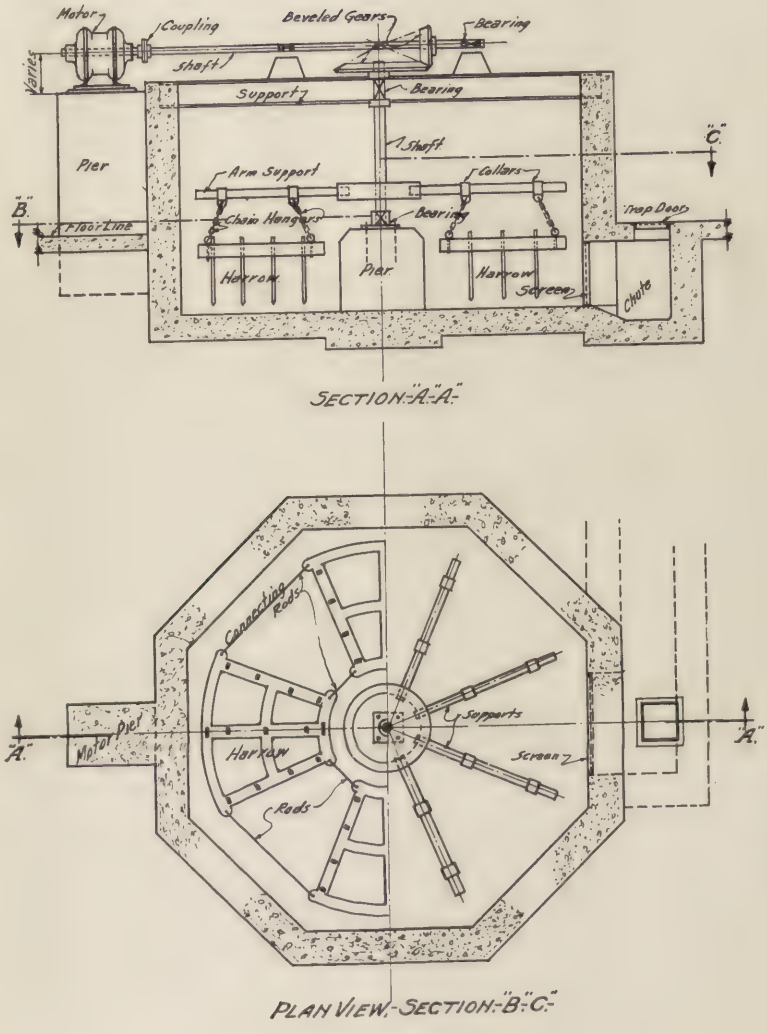


Fig. 29.—Wash-mill.

and mix it with the water. These harrows are suspended from a number of arms, which extend radially from a vertical shaft. There is generally a short pier in the center of the tank on top of which is secured a foot bearing for the vertical shaft. The upper end of the shaft revolves in a bearing which is supported by means of a frame work of structural steel. The shaft is turned by a pair of bevel gears, which may be driven either by direct connection to a motor or from a line shaft. At some point on the vertical shaft, a heavy frame work is attached and from the arms of this the harrows, which in form are somewhat similar to those used for agricultural purposes, are suspended by means of chains. The harrows do not touch the bottom and have rather long spikes or knives. The fully ground clay slip is discharged through an opening in the side of the mill. This opening is covered by a grating or screen.

The clay is usually dumped into the wash mill directly from the cars without any intermediate feed and at such a point that the clay will have to traverse the greater part of the circumference of the mill before coming to the outlet. The water is generally run into the mill in a steady stream. The clay, of course, falls to the bottom of the mill and consequently does not leave the latter until it is worked up into a fluid slip with the water by the harrows.

When clay only is worked in the wash mill, quite an excess of water is generally employed so that the clay slip usually contains from 50 to 75 per cent of water. Where the wash mill is used to handle marl and clay together, it is, of course, necessary to regulate the water much more carefully and to keep this within the limits necessary to just make a fluid slurry. Occasionally, notably in European practice, an effort is made to settle out of this slip the coarser particles. In this country, however, it is not the usual practice to do this and the slurry is fed to the grinding mills just as received fom the wash mills.

In feeding the clay slip to the grinding mills, it is, of course, necessary to regulate the quantity of this to agree with the amount of limestone going to the mill. This may be done by a

needle valve or by some arrangement similar to the "Ferris Wheel" used for feeding slurry to the kilns.[1]

Water

Except in the case where marl and clay are the raw materials, it is necessary to add water before the materials are ground. When the wet process was first employed in this country for hard raw materials, it was the practice to grind the materials dry and then to add the water just before the materials were fed to the kiln, working the mixture up in a pug mill followed by tanks containing agitators. This process was generally known as the "semi-wet" process. It did not take advantage of the possible economy of grinding the materials wet and it also required that the materials should be dried before grinding. It manifestly was not economical to take the water out and then to put it back again, so the practice of grinding dry and adding water has now been entirely discontinued (except possibly at some of the old so-called semi-wet plants) and it is now the general practice to grind the materials wet. In this case, as stated previously, the water is generally added after crushing and just before grinding. The usual practice is to add the water in a stream from a pipe at the intake of the ball mill, Kominuter, Hercules mill or Compeb mill.

A few mills are equipped with automatic arrangements for regulating the amount of water added, but the general practice is to control the amount of water by a valve on the pipe line, the mill attendant judging the proper quantity by the consistency of the slurry.

The quantity of water used varies at different mills. Some materials require very much more water to make a fluid slurry than do others and some systems of conveying and handling require the slurry to be more fluid than others. A limestone and shale mixture generally requires less water than one of marl and clay. Certain materials are more colloidal than others and swell when water is added, forming a plastic mix which requires more water to make it flow than is the case where the materials are

[1] See Chapter X.

of a more crystalline nature. Clay is, of course, colloidal and limestone crystalline. The fineness to which the material is ground also has something to do with the amount of water needed. The coarser the materials, the less water is required.

Numerous experiments have been made towards rendering the slurry more fluid by adding certain chemicals to the slurry. For instance, it is stated that the addition of a very small quantity of sodium carbonate to the slurry will have the property of making this more fluid, and consequently will allow the use of less water, which in turn would mean less fuel for burning.

It is doubtful, if the mineral and organic matter dissolved in the water, in the amounts ordinarily met with in river and well water, have any effect on either the consistency of the slurry or the properties of the resulting cement. The most common impurity in the ground waters are the salts of calcium and magnesium which, of course, are present in cement in such large quantities that the small amount introduced by the water would be negligible. Organic matter would, of course, be burned off and magnesia salts are never present in water in sufficient quantity to increase materially the percentage of this constituent in the cement. The salts of potash and soda are sometimes present in considerable quantity, notably in sea-water.

With the use of marine shells for the manufacture of cement, the question of the use of sea-water in the slurry has received considerable attention—not only because these shells are often dredged from under the surface of salt water and consequently carry to the mill a large amount of the latter, but also from the fact that at locations where shells are used, sea-water is generally the water most available for making the slurry. Ocean water contains approximately 2.9 per cent of sodium chloride. Assuming 300 pounds of water are required per barrel, means that approximately 8.7 pounds of sodium chloride are present in 900 pounds of slurry—the equivalent of one barrel of cement. If all of this soda remained in the cement, the alkalies in the latter would be increased by approximately 2.2 per cent. As a matter of fact most, if not all, of the salt is volatilized.[1]

[1] For this reaction the reader is referred to Chapter XII, on Burning, where the loss of alkalies in the kiln is discussed.

Slurry Basins

It is usual to store the slurry in large tanks or basins. There are two sets of these as previously explained—one set which receives the slurry as it is ground from the tube mill, generally called the *"correcting basins"* and the other set known as the *"mixing basins,"* holding the material ready for the kilns. The correcting basins are usually made of such size that they will receive the product from the entire battery of tube mills in the raw mill for a run of from 4 to 6 hours. There shoud be at least three and preferably more correcting basins. The mixing basins should be sufficiently large to hold the contents of from two to three correcting basins.

The correcting basins may be made of any convenient shape and of steel-plate or reinforced concrete. As the correcting basins are comparatively small, they are generally made circular in form and are placed either on or below the ground. The correcting tanks are generally set below the tube mills so that the slurry will flow into them by gravity or else may be conveyed to them by a screw conveyor. Sometimes a sump is placed below the tube mill discharge and the slurry is pumped or otherwise elevated into the basins themselves.

The mixing basins being much larger are often oval-shaped and sometimes are quite high. Reinforced concrete is usually employed for tanks of the latter shape, while round tanks may be made of this or of steel plate. An arrangement which is quite desirable on the score of economy of space, is to make the mixing basins oval-shaped and place them underneath the kilns, since this is not only a convenient location for them but it is one which cannot be used for other operations. Occasionally the mixing tanks are placed quite high so that they will feed into the kilns directly without the use of a pump.

Slurry must be kept in constant agitation and this may be done by a number of different devices. The oldest form consists of a paddle agitator and these are still very much used. Compressed air is also employed and this is particularly desirable where the tanks are of small diameter and high. The newer plants are in-

stalling the Dorr Slurry Mixer.

For stirring round tanks the ordinary paddle agitator is probably more used than anything else and this is, therefore, the form of agitator which is generally used in the correcting basins. Thorough mixing is not very necessary here and the main object of the agitator is to prevent settling. Fig. 30 shows the ordinary type of round correcting basin and agitator.

Oblong basins are usually stirred by three or more agitators. (See Fig. 31) the arms of which are so arranged as to pass by each other as will be indicated by referring to the drawing. The agitators are all revolved from a common shaft which may be direct connected to a motor through a flexible coupling or driven from a line shaft.

As will be seen by referring to the plan, the objection to this type of agitator is that there are small sections of the basin which are not reached by the arms and consequently which are not mixed. It has been found good practice to agitate this portion of the tank by dropping a pipe to the bottom of the tank at the points indicated and blowing with compressed air.

The mechanical agitators are usually supported on structural steel beams or on reinforced concrete girders. The vertical shafts are usually provided with step bearings athough the weight of the shaft is generally taken care of by means of a collar resting on the top bearing. The arms are usually made of channel iron and are secured to the shaft by means of a casting. There are generally four arms on a shaft and they are arranged in pairs at right angles to each other as indicated.

Compressed air is used for agitation at many plants. It is generally the practice in this case to employ a tall narrow tank with a conical bottom and to agitate by blowing air in at the apex of the inverted cone. Compressed air is an efficient method of agitation provided enough air is used. It, however, requires more power to agitate with compressed air than with other forms of agitators.

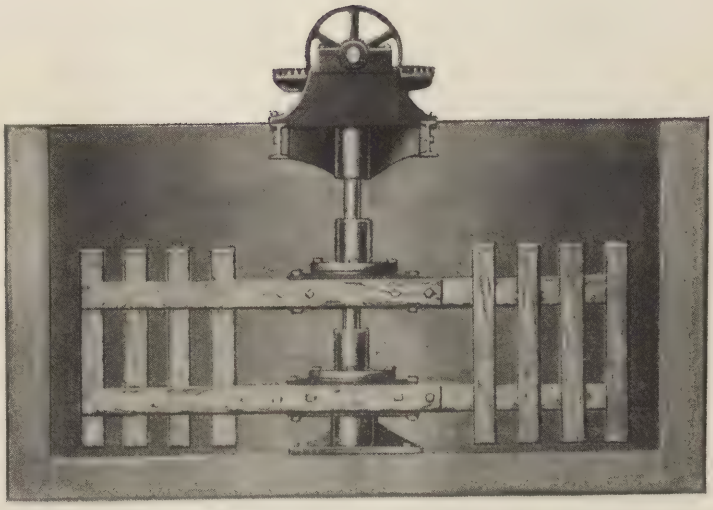


Fig. 30.—Slurry basin with one agitator. Elevation.

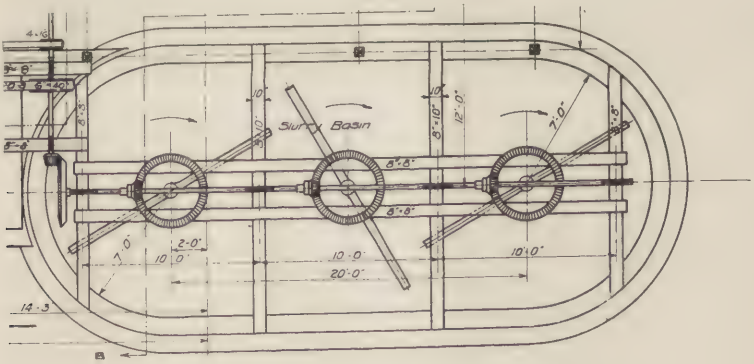


Fig. 31.—Large slurry basin with three agitators. Plan.

Dorr Slurry Mixer

The Dorr slurry mixer is probably most desirable as it is not only a good agitator, but also an efficient mixer. It is being used quite generally in the newer cement plants for mixing slurry.

The Dorr slurry mixer, Figs. 32 and 33 depends for its efficiency upon a redistribution of the slurry in the basin and not

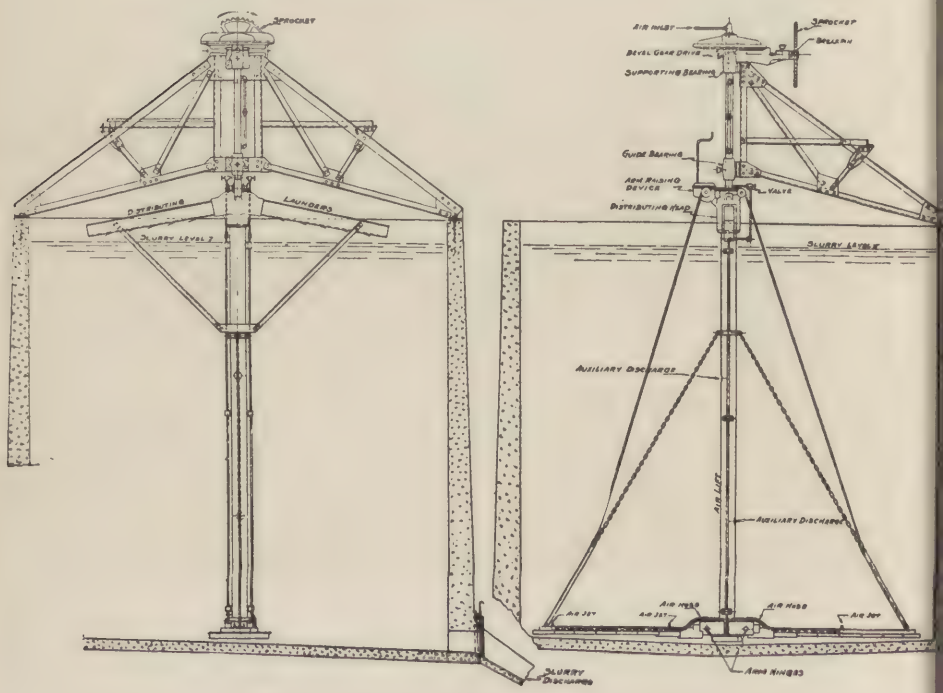


Fig. 32.—General arrangement of Dorr slurry mixer.

upon swirling the contents of the tank. The apparatus consists of a hollow vertical shaft extending downward through the middle of the basin to almost the bottom of the latter. This shaft is supported by a rigid "A" frame to which are attached the two bearings in which the shaft revolves and at the top of which are located the bevel gears actuating the shaft. No step bearing is employed. To the lower end of the shaft, are fixed two radial

arms with plow blades. The latter move the slurry towards the center of the basin. The shaft as stated is hollow and the slurry is made to flow up through this by means of an air lift. The slurry overflowing at the top of this hollow shaft, is caught by two radial launders or troughs which revolve with the shaft. These launders distribute the slurry uniformly over the surface of the basin . The hollow shaft is provided with auxiliary discharge openings so that the slurry is distributed at different

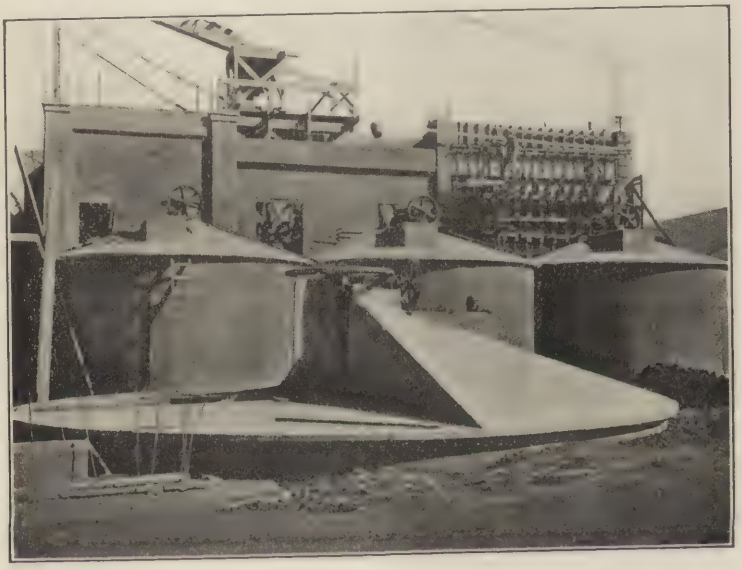


Fig. 33.—Dorr slurry mixers—Oklahoma Portland Cement Co., Ada, Okla.

elevations and circulation is maintained when the basin is only partly filled. The plow arms are also provided with air jets so as to provide vertical mixing throughout the basin.

The mixer revolves at from one to three revolutions per minute according to the size of the basin; from which it is evident that mechanical agitation is not depended upon for the mixing. Instead this is secured by the distribution of the slurry through the launders and with the help of the air jets in the radical arms

at the bottom. The advantages claimed for the Dorr Mixer are thorough mixing, low power, low upkeep due to all bearings being out of the slurry, etc.

The Dorr mixer requires about one-half horsepower per 1,000 cubic feet of basin capacity for revolving the mechanism and about the same amount for compressing the air. Both the quantity and pressure of the air depend on the intensity of agitation required, viscosity of the slurry, size of basin, etc. The air pressure depends on the depth of the basin but generally for a basin less than 20 feet deep is from 10 to 25 pounds gauge pressure. The quantity of air required varies from 4 to 10 cubic feet per minute per 1,000 cubic feet of basin capacity.

As an example of an actual installation, in a basin 20 feet in diameter by 12 feet deep holding 3,770 cubic feet of slurry the Dorr Mixer required 17.3 cubic feet free air per minute at 17.5 pounds gauge pressure and 3.1 horsepower to operate.

Handling the Slurry

For handling slurry four methods are in common use, (1) plunger pumps, (2) compressed air lifts, (3) centrifugal pumps, and (4) elevators and conveyors.

Quite a number of plants employ for handling the slurry, bucket elevators and screw conveyors similar in every respect to those which are employed for handling fine dry materials. As far as the operation goes, this equipment is perfectly satisfactory. It is, however, much more expensive to install and takes up a great deal more room than do the pumps and air lifts.

Screw conveyors are often placed in troughs to keep the slurry moving since the trough would otherwise have to be pitched at a considerable angle in order to avoid settling. When no elevating of the slurry has to be done and a short straight line conveyor can be employed this is good practice.

Plunger pumps with ball valves are used to some extent for handling slurry, particularly in the older plants in this country and in Europe. Fig. 34 shows such a pump of American design, manufactured by the Bonnot Company. Its action is similar to

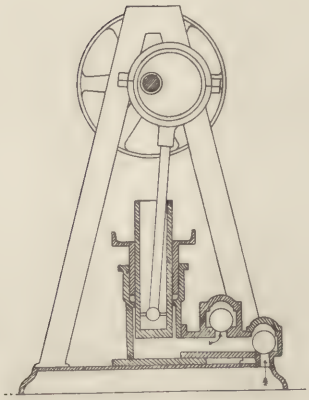


Fig. 34.—Ball valve slurry or marl pump.

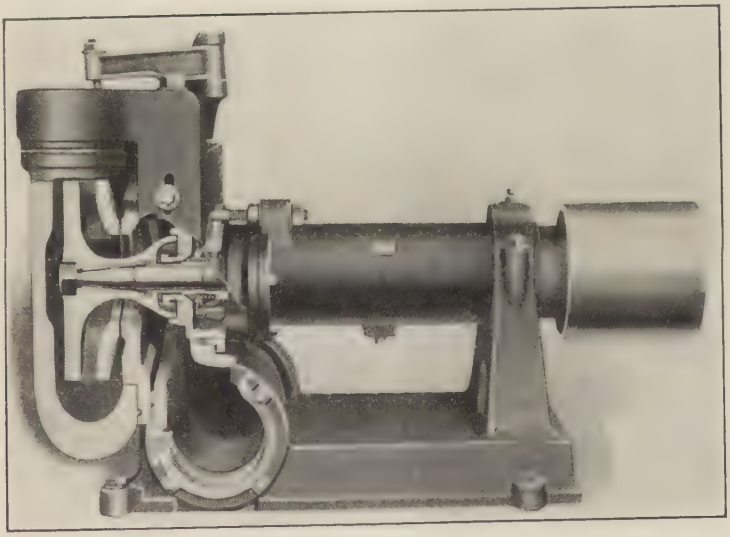


Fig. 35.—Wilfley sand pump for pumping slurry.

that of other plunger pumps and the operation of the valves will be evident from the cut.

The plunger pumps are now generally being displaced by centrifugal pumps. The latter are very compact and may be driven by direct connection to a motor. The Wilfley Sand Pump, which has been extensively used for moving tailings and pulp in metallurgical plants, is now being much used in cement plants. This pump is shown in Fig. 35. The advantage of this pump is that no stuffing box is required as is the case with the ordinary centrifugal pump where such a device is necessary in order to prevent the material from leaking out where the shaft projects from the pump. The stuffing box causes wear on the shaft when gritty materials are handled. In the Wilfley pump, a centrifugal seal takes the place of the stuffing box. This seal consists of a revolving member called an "expeller" having paddles radiating from a recess in its center to its periphery and a stationary member which has a projecting groove. The revolving member is cast *in integral* with the runner and is set close to the stationary member which acts also as a side wearing plate. In action, the slurry is prevented from leaking out by the centrifugal action of the wings of the expeller, similar to that of an open runner, and any slippage by the side is caught by the projecting groove and delivered to the wings. A check off valve seals around the shaft while the pump is not in action.

The Allis-Chalmers slurry pump is an air lift and is shown in Fig. 36. It is an adaption of the "blow case" used in chemical plants. It consists of two receiving or "blow-tanks" which are set side by side and into which the slurry flows by gravity. Each tank is equipped with a float which operates an air valve. The slurry entering the tank raises the float and when the tank is full this float opens the air valve allowing compressed air to flow into the tank. This in turn forces the slurry out of the tank and to whatever elevation is desired. This lift has the advantage of having no moving parts, but the disadvantage of taking up considerable floor space. The top of the blow tanks must also be below the level of the bottom of the slurry basins.

The air jet lift has also been employed for lifting slurry.

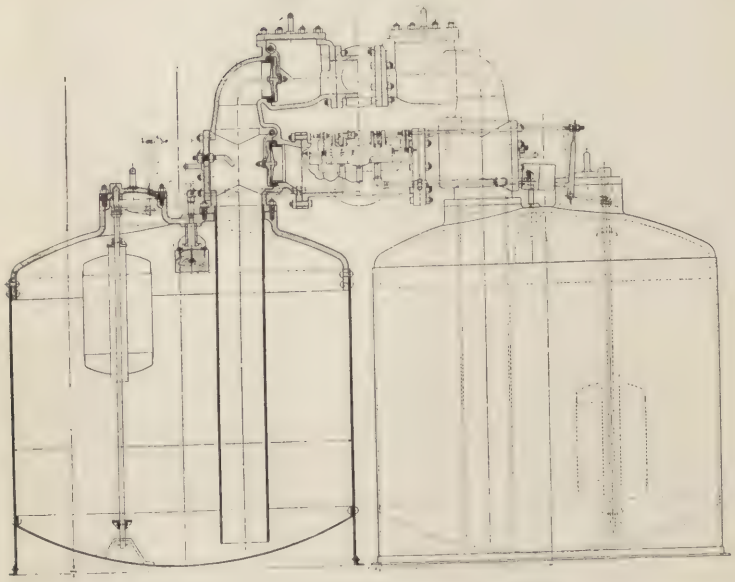


Fig. 36.—Allis-Chalmers air slurry pump.

Weight of Slurry

The weight of cement slurry varies considerably, depending principally on the amount of water it contains and also to a slight extent on the nature of the solid material itself.

For estimating the capacity of tanks, the horsepower to move the slurry, etc., it may be taken as weighing approximately 105 pounds per cubic foot, having an apparent specific gravity of 1.7 and one cubic foot containing 65 pounds of dry raw material. Table XIV gives an idea of the variation in weight, etc., with varying percentages of water. The actual weight may be found in the laboratory by weighing a marked liter flask empty; and then filled to the mark first with the slurry and then with water, or *visa versa*. The weight of a cubic foot of slurry will then be—

$$\frac{F - S}{C - S} \times 62.43 = W$$

When

F = weight of flask filled with slurry.
S = weight of flask empty.
C = weight of flask filled with water.
W = weight of one cubic foot of slurry.

Complete Grinding Plant

Fig. 37 shows the raw mill of a modern wet process cement plant. This is equipped with ball and tube mills but only the tube

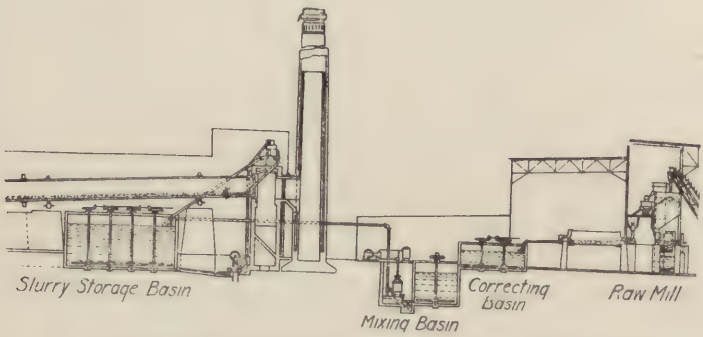


Fig. 37.—Raw mill—Pyramid Portland Cement Co., Des Moines, Ia.

mills and slurry tanks are shown. The installation of Compeb mills would be essentially as shown.

TABLE XIV.—Weight of Cement Slurry, Weight of Solids per Cubic Foot, Density, Etc.

Water per cent by weight	Solids per cent by weight	Water per cu. ft. slurry Lbs.	Solids per cu. ft slurry Lbs.	Weight per cu. ft. Lbs.	Apparent density Water = 1	Slurry per bbl. cement Cu. ft.
30	70	32.7	76.2	108.9	1.75	8.0
31	69	33.3	74.3	107.6	1.72	8.1
32	68	34.1	72.4	106.5	1.70	8.3
33	67	34.8	70.6	105.4	1.69	8.5
34	66	35.5	68.8	104.3	1.67	8.7
35	65	36.1	67.1	103.2	1.65	8.9
36	64	36.8	65.4	102.2	1.64	9.2
37	63	37.4	63.8	101.2	1.63	9.4
38	62	38.1	62.2	100.3	1.62	9.7
39	61	38.8	60.6	99.4	1.59	9.9
40	60	39.4	59.0	98.4	1.58	10.2

CHAPTER IX

CRUSHING MACHINERY

Development of Grinding Machinery

In the early days of the industry when the plants were small, manufacturing only a few thousand barrels a year each, both the raw rock and the clinker were ground with mill stones, just as corn is ground in the small water-power mills familiar to every one. The first advance upon this was to encase the stones, and as the American manufacturers began to work up a home market for their product and to increase their output to meet the demand, they also began to experiment with a view to securing more efficient pulverizers than the mill stones. As a result of their experiments, the Atlas Portland Cement Co. patented the Huntington mill which they still use. In 1889 the American Cement Co. installed a Griffin mill in their plant at Egypt and this mill is still in use there, and in many other large plants throughout the country. Another system of grinding consisting of a ball mill for the coarse grinding and a tube mill for the final pulverization was introduced about this time by the Bonneville Cement Co. in their plant at Siegfried, Pa., and this combination also came into prominent use in the industry.

Newer types of pulverizers are the Kominuter, The Fuller-Lehigh Pulverizer, the Raymond Roller Mill, the Bonnot Mill, the Kent or Maxecon Mills, the Sturtevant Ring Roll Pulverizer, the Bradley-Hercules Mill, the Allis-Chalmers Compeb Mill, etc. All of these mills have been extensively used in the cement industry. The Fuller-Lehigh Mill and the Raymond Mill are used now chiefly for pulverizing coal, practically all cement plants employing either one or the other mill. A few plants use the Bonnot Mill for this purpose. Ring Roll Mills are still used to some extent for preparing for tube mills; the newer plants, however, are being chiefly equipped with (1) Hercules Mills followed by Tube Mills, (2) Kominuters followed by Tube Mills, or (3) Compeb

Mills alone. These combinations are suitable for grinding both the raw material and the clinker and to both wet and dry grinding.

In the use of any of the above mills upon dry raw materials, it is necessary to break up the material to a size which will permit the material to be fed to the mills. In order to do this, as has been stated, crushers of the gyratory, jaw or roll-jaw type are usually employed, as the first stage in this preliminary reduction. The gyratory crusher was developed by the Gates Iron Works, Chicago, but is now made and sold by several firms. This type of crusher was used in cement mills almost exclusively until about 1914 when large size jaw crushers began to receive attention. About the same time the Allis-Chalmers Co. brought out the Fairmount Crusher (Roll-jaw) and this proved satisfactory where the limestone was not too tough. The opportunity for the jaw and roll-jaw crushers was made by the rise in the wage paid labor and the introduction of steam shovels to take the place of hand loading in most quarries incident thereto. This change made it necessary to employ crushers which would handle large pieces of rock. For the same capacity, the jaw and roll-jaw crushers will take much larger stone than will the gyratory crushers; although in other respects probably not so desirable as the latter.

At most mills, particularly where large size crushers are employed for breaking down the rock as received from the quarry, it is necessary to follow the primary crusher by a secondary breaker. These latter are now generally of the "hammer mill" type. Small gyratory crushers and rolls are also used to a limited extent for this purpose. The large primary crushers generally reduce the limestone to 6 to 8 inches and under, while the secondary crushers reduce this product to such size as can be handled by the granulators or pulverizer, usually to at least 2 inches and under.

Clay is generally handled as received from the bank by wash mills, if the wet process is employed, or by edge runner mills if the dry process is used. Hammer mills are employed for shale.

Below will be found descriptions of various types of crushers, pulverizers, etc., used in cement mills for preparing the raw material for the kilns and for grinding clinker. The Raymond and Fuller-Lehigh Mills which are used chiefly for pulverizing coal are described in the section on fuel.

Gyratory Crusher

Fig. 38 shows a section of a gyratory crusher and Fig. 39 a view of this. Referring to the former illustration, it will be seen

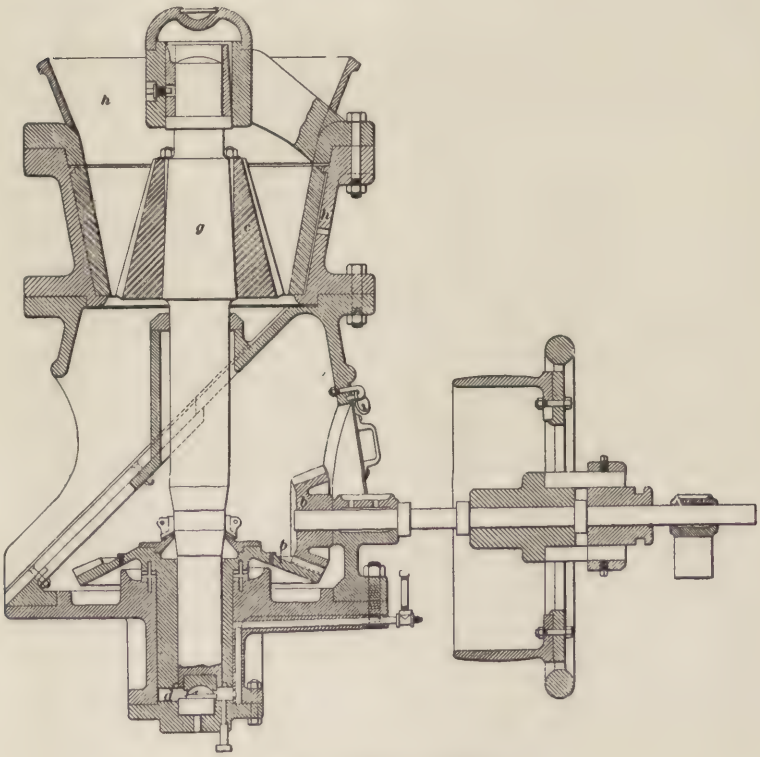


Fig. 38.—Gyratory crusher.

that the outer shell of this type of crusher resembles an hour-glass somewhat in shape. It is open at the top for receiving the

stone and is provided with an inclined spout at its lower lobe for discharging the crushed rock. The main shaft, *g*, is suspended from a spider that spans the top of the opening and extends downward through the throat, *h*, to a step bearing, *d*, in the base. A conical shaped crushing head, *c*, is keyed to the shaft where this passes through the throat. The throat is lined with plates

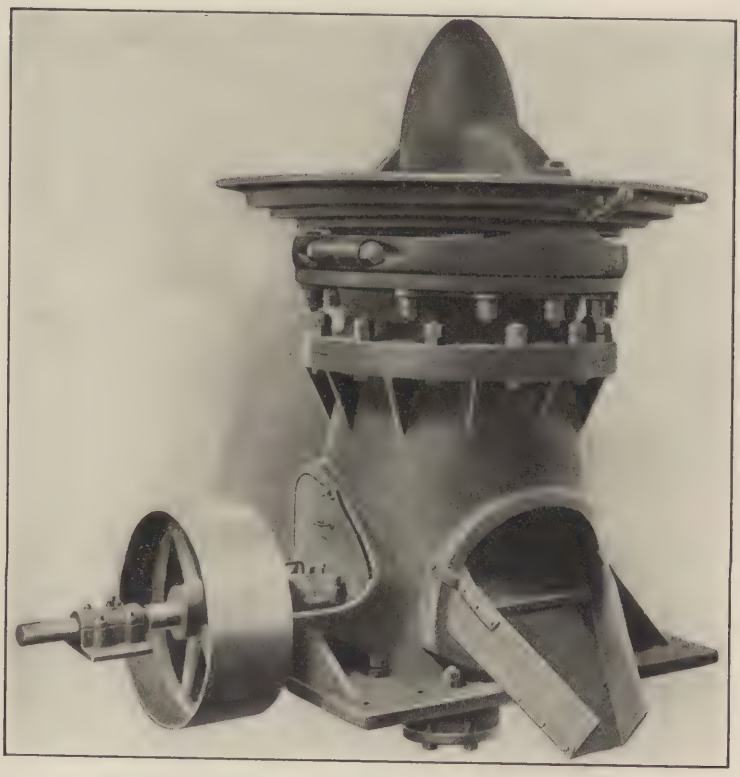


Fig. 39.—Large gyratory crusher—Allis-Chalmers Mfg. Co.

of some hard tough metal such as chilled-iron, manganese steel, etc., and the crushing head also is made of such a material. The crushing is done in the annular space between the head and the throat plates. The lower end of the shaft passes through a sleeve

which is bored off center one-half the required gyration, to form an eccentric, and this sleeve is driven by a pair of bevels, *b*, which in turn receive their power through the pulley to the right of the machine. The main shaft being centrally held in the spider at its upper end and slightly off center in the eccentric at its lower, the axis of the shaft describes a cone as it revolves causing the crushing head alternately to approach and recede from the throat plates. This action causes the breaking of the material, which as it is crushed drops further down into the throat and finally out of the machine by means of the discharge spout. The largest motion is, of course, at the bottom of the throat and the degree of motion here is the "throw" or "stroke" of the crusher. The spindle receives no direct rotating motion from the shaft and is held loosely in the eccentric. The number of revolutions of the eccentric and the number of strokes correspond. These vary with the make, size of the crusher, etc., but are seldom more than 250 revolutions per minute. The throw also varies but is generally only a fraction of an inch.

The crushing is done in all parts of the throat and hence is continuous. For this reason the gyratory crusher is steady in the power required and has large capacity. On account of the sidewise rolling of the head upon the concaves it is also less liable to choke than the ordinary jaw crusher.

The main shaft is adjustable and can be raised or lowered by means of the step bearing, *d*. By raising, the opening between the bottom of the throat and the crushing head is decreased in width and this in turn gives a smaller product, and *vice versa* by lowering, a larger product. This arrangement also allows wear in the crushing head and plates to be taken up.

The gyratory crusher is made in sizes ranging from laboratory grinders to machines having a capacity of several thousand tons an hour. Table XV gives information about the capacities, weights, etc., of crushers of this type. The sizes now generally employed in cement mills range from the No. 9 to the No. 24. The former size is, however, somewhat small for a modern cement mill. It has enough capacity for the average mill but the annular receiving opening is not wide enough to take in the

large blocks of stone which a steam shovel will handle, making it necessary to blast or sledge these into smaller pieces in the quarry before sending them to the mill. Most of the newer mills are equipped with the Nos. 18, 21 or 24 crushers. A No. 18 crusher will handle blocks approximately 36 x 36 inches and the No. 24 blocks 48 x 48 inches.

The No. 5 and 6 crushers set to give a product from 2 to 3 inches, are sometimes employed after the large crusher to crush the product of the latter small enough to be fed to Kominuters, Hercules Mills, etc., but hammer mills are now more often used for this purpose.

TABLE XV.—Sizes, Capacities, Weights, Etc., of Gyratory Crushers[1]

Size of crusher	Size of each feed opening Inches	Approx. capacity		Horse power to operate	Shipping weight Pounds	Shovel dipper rated capacity in cu. yds.[2]
		Size of product Inches	Tons per hour			
9	20 x 80	4	250	100-150	93,000	Not satisfactory for shovel work
7½	14 x 55	2½	75	50-75	38,000	
6	12 x 46	2½	50	30-45	28,000	
12	26 x 100	6½	525	125-200	153,000	2
18	36 x 136	8	1,056	150-250	300,000	2½
21	42 x 153	8½	1,581	175-275	360,000	3
24	48 x 166	9	1,890	200-350	500,000	4

Gates crushers are well adapted for free feeding or feeding directly from cars, as the rock can be fed into them from all directions.

Fig. 18 shows a large gyratory installed in a cement plant.

Jaw Crusher

The Jaw or Blake crusher is shown in Fig. 40. It consists of a heavy frame usually of cast steel or semi-steel in which is suspended a movable jaw plate *b*. Opposite this movable plate is a fixed plate, *a*, and the crushing is done between these two jaws, *a* and *b*. The jaw *b* is given a reciprocating motion by means of an eccentrically operated vertical pitman, *d*, and two

[1] Information from Catalogue of Traylor Engineering and Manufacturing Company, Allentown, Pa. Crushers of different makes vary somewhat in size of opening, weights, etc.

[2] A crusher of the size given will take the largest stone which will pass through a dipper of this capacity or smaller.

toggles, *c* and *c*. It will be seen by referring to Fig. 40 that as the shaft, *f*, revolves the pitman is alternately raised and lowered by the eccentric, *e*. This upward motion of the pitman, in turn, straightens out the toggles and moves the swing jaw nearer to the fixed jaw. The rod, *g*, pulls the swing jaw back against the toggles during the return stroke.

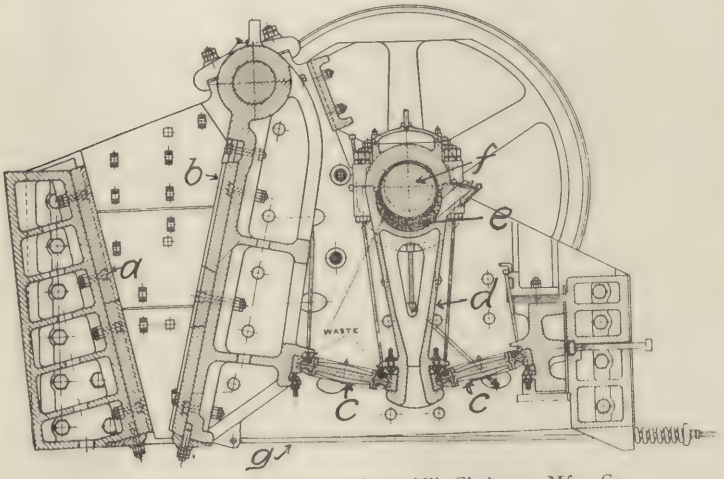


Fig. 40.—Section of jaw crusher—Allis-Chalmers Mfg. Co.

The angle between the jaws must be small enough to nip the rock but large enough to give capacity at the mouth without having excessively long jaws. This angle in large crushers is usually about 25° and the fixed jaw is often nearly perpendicular. The number of effective strokes is the same as the number of revolutions of the pulley, since no crushing is done on the return stroke. Half the time is occupied, therefore, in storing up energy in the fly wheels. The movement at the bottom of the jaws or throat is the "stroke" or "throw" of the crusher. This can be adjusted by means of different size toggle plates and sometimes by means of wedge plates against which the rear toggle presses

The jaw plates are usually ribbed and are made of chilled iron or manganese steel. They are made renewable. The lubrication

of this type of crusher is important and usually a forced feed and filtering system is employed.

The Blake crusher will take a rock the full size of the receiving opening and reduce the same to pieces not larger than the maximum opening at the throat. The size of the crusher is usually designated by the dimensions of the receiving opening. Blake crushers are well adapted to hard rock which breaks up into cubical pieces, but are less desirable for soft material and limestone which breaks in the form of slabs. The size jaw crushers usually employed in cement mills, weights, capacities, etc., are given below.

TABLE XVI.—SIZE, WEIGHT, CAPACITY, ETC., OF LARGE JAW CRUSHERS[1]

Size in inches	Approx. capacity— Size product Inches	Tons per hour	Horse-power to operate	Shipping weight Pounds	Shovel dipper [2] rated capacity in cubic yards
36 x 42	6	144	115	116,000	1½
42 x 48	8	260	150	155,000	1¾ to 2
48 x 60	10	713	180	215,000	2½ to 3½
56 x 72	10	740	230	310,000	4
66 x 86	12	1,110	300	460,000	5

Fairmount or Roll-Jaw Crusher

The Fairmount crusher[1] is much used for crushing cement-rock and soft limestone. This crusher is illustrated in Fig. 41. Referring to the illustration it will be seen that the crushing is done between a toothed roll, *a*, and a curved jaw or anvil, *b*. The latter is generally stationary, but can move backward under very heavy pressure as it is held in position by heavy steel tie rods, *c*, which pull against a powerful nest of heavy springs. This arrangement allows the jaw to take up or equalize the ex-

[1] Information from Catalogue of Traylor Engineering and Manufacturing Company, Allentown, Pa.

[2] A crusher of the size given will take the largest stone which will pass through a dipper of this capacity or smaller. The first two crushers have a greater capacity than the shovels equipped with 1½ to 2-yard dippers respectively.

[1] Allis-Chalmers Mfg. Company., Milwaukee, Wis.; The Pennsylvania Crusher Company, Philadelphia, make a somewhat similar crusher.

cessive shocks and pressures met with in this type of crusher. The roll, *a*, is provided with teeth and is so located with relation to the jaw that the preliminary fracturing of the large pieces of rock fed to the crusher is effected by the sledging action of these

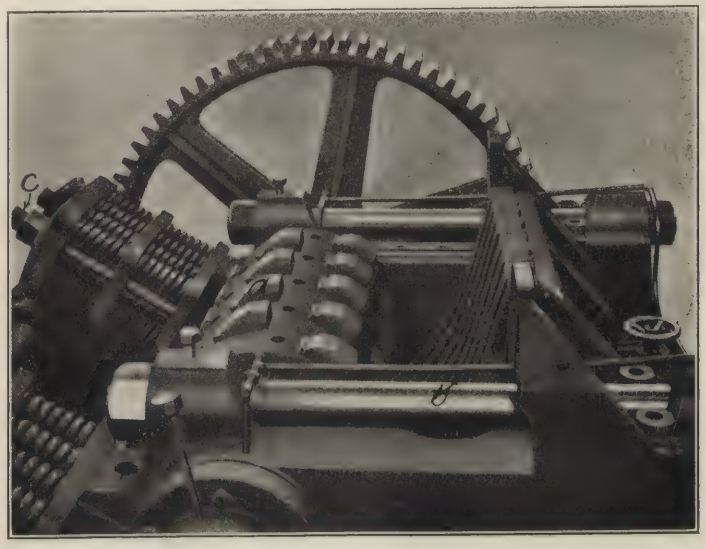


Fig. 41.—Fairmount "roll-jaw" crusher, with hopper removed—Allis-Chalmers Manufacturing Co.

teeth on the rock as it rests by gravity upon the roll. This action is intensified by having the teeth of different heights. Further crushing of the rock is accomplished by a direct nipping and crushing action between the roll and the jaw.

The effect of the roll is to forcibly discharge the material when crushed and also to get rid rapidly of fines which may be fed to it along with boulders. For this reason the Fairmount crusher is particularly well adapted to crushing limestone containing clay or shale seams or other soft, sticky material.

The jaw is lined with chilled iron ribbed plates. The teeth on the roll are removable and hence may be replaced when worn down or broken.

The Fairmount crusher is made in three sizes, 24 inches x 60 inches, 36 inches x 60 inches and 60 inches x 84 inches.

Hammer Mill

The hammer mill is made in a number of forms, each maker having his own type of mill and peculiarity of construction. In some, the hammers are fixed and in some hinged, while in one form rings take the place of hammers. The form shown in Fig. 42 is the Williams Mill,[1] while Fig. 43 is the "Pennsylvania Super" Hammer Mill.[2] This is one of the best of this type of granulator. It consists of a number of hinged hammers, which revolve around a horizontal shaft called the "rotor." These hammers crush the material and pass it out through a grid screen as shown in the cut. There are usually from eight to ten rows of hammers and eight to twenty-seven hammers to the row. The regulation of the size of the product is by means of spacing between the bars of this grid.

The hammer mill as now made is provided with an arrangement by which the grinding plates can be moved nearer the hammers, usually by means of a rack and pinion operated by a hand wheel on the outside, to take up the wear of the hammers.

Other mills of this type are the "Jeffrey[3] Swing Hammer Pulverizer," and the "K. B. Mill."[4] In the latter, hinged bars take the place of hammers.

Mills of this type have been employed to some extent in place of ball mills, particularly where these latter are designed to prepare for Fuller-Lehigh or Griffin Mills, as the installation is not only much cheaper of itself but considerable building and bin space is saved thereby.

At a few cement plants, mills of the swing hammer type are also used in connection with some form of outside separator such as the Newaygo (see page 236) to prepare material for the tube mill. They compare favorably with Ball mills for this purpose in

[1] Williams Patent Crusher and Pulverizer Company, St. Louis, Mo.

[2] Pennsylvania Crusher Company, Philadelphia, Pa.

[3] Jeffrey Manufacturing Company, Columbus, Ohio.

[4] K. B. Pulverizer Corporation, New York, N. Y.

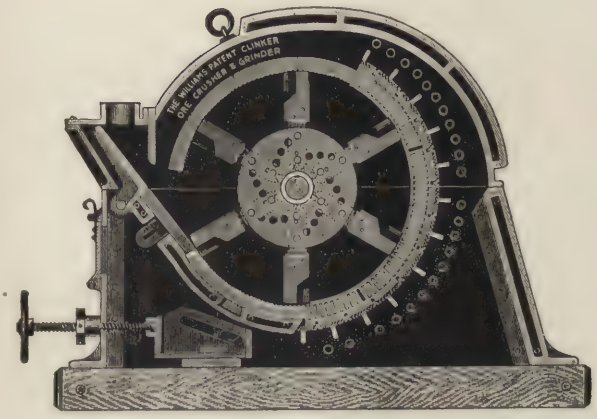


Fig. 42.—Williams mill.

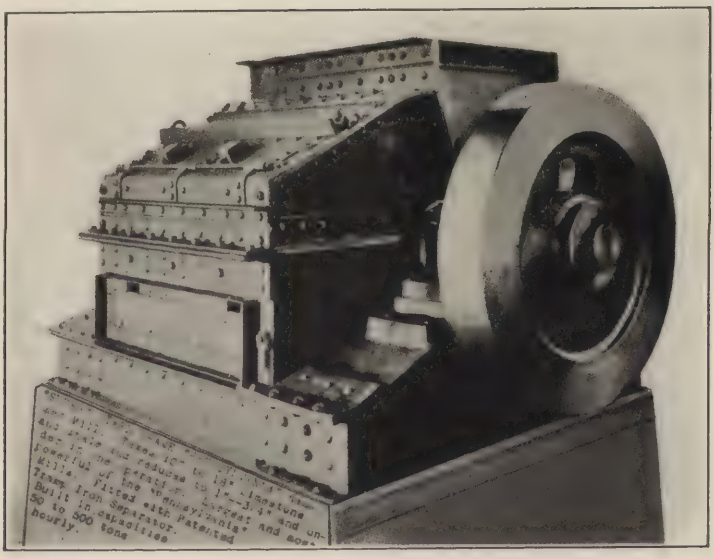


Fig. 43.—Hammer mill—Pennsylvania Crusher Co.

point of both power consumed and output but are not so efficient as the newer Hercules mill.

Hammer mills are also used quite generally for the primary crushing of shale. This type of mill is well adapted to this. At a few plants, very large hammer mills have been employed in place of large crushers for primary crushing of limestone.

The chief employment of large hammer mills is now to replace the small crushers (No. 5) when these latter are used after a large crusher. Hammer mills are now made with a capacity of from 100-250 tons of limestone per hour, reducing this from pieces 10 inches and under down to material passing a 2-inch screen. Such material is suitable without further reduction, to be fed to Hercules mills, Compeb mills or Kominuters.

Hammer mills are made in a great range of size. Some of the large mills used in connection with the primary jaw or gyratory crushers having capacities comparable with these. As is the case with all crushers and grinders, the capacities vary not only with the size mill, but also with the hardness or brittleness of the material to be reduced and the size product desired. The following figures are by way of illustration only.

When preparing for a tube mill the No. 3 Williams mill will grind from 8 to 10 tons per hour to a fineness of 95 per cent passing the No. 20 sieve taking pieces 1½ inches in size with an expenditure of from 45 to 55 horsepower and a repair cost of from 1¼ to 2 cents per ton (0.4 to 0.6 cent per barrel of cement).

When used for secondary crushing a No. 12 Pennsylvania "Super" Hammer mill will take the product of a Fairmount crusher consisting of pieces of rock 10 inches and under and reduce this to 2 inches and under at the rate of 250 tons per hour. This mill requires about 200 h. p. where operating at full capacity.

The repairs on a hammer mill vary with the hardness of the material crushed, the amount of flint or silica in this, the size of the product, type of mill employed, care in operation, etc., but are usually from 0.15 to 2.0 cents per ton of material reduced; the former figure representing repairs where the machine is used for secondary reduction (from 10-inch to 2-inch) and the latter

figure the repair cost when the hammer mill is used to prepare for the tube mill.

Hammer mills are usually provided with what is known as a "tramp-iron" separator. This consists of a compartment into which large pieces of iron which find their way into the mill are thrown; otherwise the entrance of a coupling pin or spike into the mill would result in broken hammers, etc.

Hammer mills may be driven in any appropriate way such as by a belt from a line shaft or motor. The most approved method, however, is by means of a motor of proper speed, direct connected to the shaft of the mill by a flexible coupling.

When Hammer mills are employed to prepare material for a tube mill, they are usually fed from an overhead bin by means of some arrangement which will give a uniform feed. When used for secondary crushing they are often fed directly from the primary crusher. (See page 135.)

Table XVII gives information about Pennsylvania Hammer Mills, and is taken from the catalogue of the manufacturers of these. An idea can be obtained from this as to the outputs, horsepower required, etc., of hammer mills of various sizes.

TABLE XVII.—Size, Capacity, Weight, Etc., of Pennsylvania Hammer Mills

Size	Hopper Length	Hopper Width	Capacity (approx.) (a)	H. P. (approx.) (b)	Weight (approx.)	Hammers Dia. circ.	Hammers Rows	Hammers No.	Speed (rpm)
SX- 5	2'-3½"	1'-6"	55- 70	80- 90	12,500	42"	8	80	800-50
SX- 6	2'-9 "	1'-6"	70- 85	100-115	13,500	42"	8	104	800-50
SX- 7	3'-2½"	1'-6"	85-105	125-145	14,500	42"	8	128	800-50
SX- 8	3'-8 "	1'-6"	100-125	150-175	15,500	42"	8	152	800-50
SX- 9	4'-1½"	1'-6"	115-145	175-200	16,500	42"	8	176	800-50
SX-12	3'-8½"	1'-7"	150-190	225-250	36,500	58"	10	180	720-50
SX-13	4'-2 "	1'-7"	175-220	265-300	38,500	58"	10	210	720-50
SX-14	4'-7½"	1'-7"	200-250	300-350	40,500	58"	10	240	720-50
SX-15	5'-1 "	1'-7"	225-285	340-400	42,500	58"	10	270	720-50

(*a*) CAPACITIES—These will vary widely with the size and kind of feed, hardness, structure, moisture content and fineness of crushing. The capacity figures therefore show the minimum and maximum range.

(*b*) HORSEPOWER—These approximate Horsepowers represent Motor sizes but they will change with the varying conditions.

Edge Runner Mill

The edge runner (Fig. 44) is made in two different types and under the names "Edge Runner Mills," "Chaser Mills," "Chillean Mill," "Dry Pan" and "Wet Pan," according as used for wet or

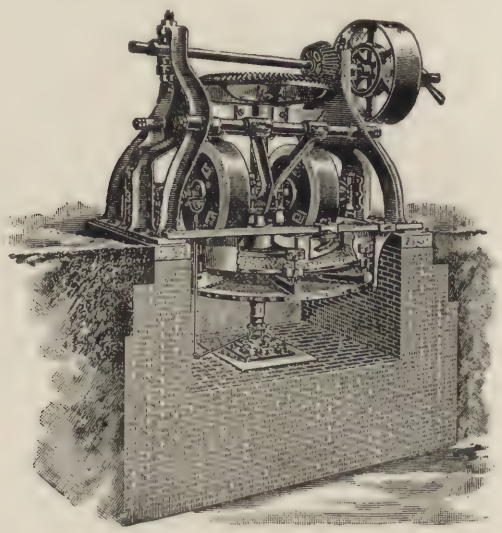


Fig. 44.—Edge Runner Mill.

dry grinding. It consists of a pan in which revolve one or more rollers. Either the pan itself or the rollers may be driven. In the one form, the pan is driven and the rollers are revolved by friction with the former. In another type, the pan remains stationary and the rolls are driven around. This latter type of mill, however, is much less employed than the former and usually only in cases where the nature of the material would allow slipping of the rollers as in grinding paints and colors in oil. Both the pan and runners are usually made of cast iron. The mill grinds by the weight of the rolls acting on the particles to be ground. Chilled iron or steel scrapers or plows keep the material to be ground under the rolls as the pan revolves. Where the material is to be ground to a definite size, the pan bottom is often fitted

with steel or chilled iron grids through which the fully ground material passes while the unground is scraped back under the rollers by means of scrapers.

Edge Runner mills are not employed to any extent in dry process plants, but are often used in wet process plants to crush shale and sometimes for the secondary crushing of limestone. They can be used to reduce shale from quarry size to Kominuter or Compeb mill feed. They consume a relatively large amount of power for the amount of crushing done and can generally, even in wet process plants, be replaced to advantage by more efficient equipment. Wet pans have the advantage that material to be crushed can be fed into them in large quantity at once, and hence small cars of shale can be dumped directly into them.

Rolls

Crushing rolls which are quite popular in metallurgical work have never been employed to any extent in the cement industry. This is probably due to the fact that, when required to make too great a reduction, the rolls must be unusually large if they are to work efficiently. Thus a set of 72-inch diameter rolls should not be fed material larger than 2.9 inches plus the distance between the roll faces ("spread" of the rolls). Assuming the rolls are to crush to 2-inch and under, it will be seen from this that the material fed to the rolls should not be greater than 4.9 inches. A much less costly hammer mill than the above set of rolls will take 10-inch material and reduce to 2 inches, which probably accounts for the almost universal employment of the latter instead of rolls for secondary crushing. Rolls also, in spite of their apparent simplicity, require more than ordinary attention to keep them in good working condition. They must be fed the material to be crushed very uniformly and over the whole surface of the roll, the roll faces wear unevenly, the bearings require much lubrication and the springs frequent adjustment.

Fig. 45 shows a set of crushing rolls, the rolls themselves being only indicated by the dotted circles.

Referring to Fig. 45 which represents the machine without its dust covers and automatic feed: *A* represents the main frame,

having the journals for the stationary rolls cast on in one piece. *B* is the movable journal which is held in the center of the frame,

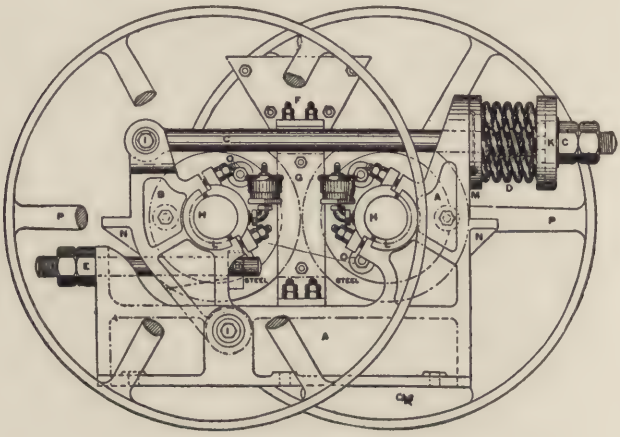


Fig. 45.—Set of crushing rolls.

A, by means of a heavy steel shaft, *I*, which passes entirely through the frame. The swinging journals are held in place by the tension rods, *C*, to which are attached nests of powerful coiled springs, *D*, held in position by the washers *M* and *K*. The springs are stiff enough to resist the pressure imposed upon them by ordinary crushing without compression, and yield only under abnormal strains, due to the accidental passage through the rolls of foreign substances, too hard to crush, such as broken drill points, etc.

The power is applied to the rolls by means of the pulleys, *P*. and *P*. Both rolls are direct driven. In some form of rolls gears are used, and one roll is driven from the other by means of these. These gears, however, are liable to wear out rapidly from the grit, etc., which always finds its way into them. Sometimes only one roll is driven. The rolls usually revolve at a surface speed of from 600 to 1,000 feet per minute.

Rolls are often supplied with automatic feeds to regulate the stream of material passing through them. They are also usually enclosed in a dust-proof casing.

The diameter of rolls required to make a given reduction is determined by the maximum size of feed which can be nipped by the rolls without slippage. This size is calculated by the formula $X = 0.08\,R + T$. Where X is the maximum size feed, R = radius of the roll in inches and T the spread of the roll. The capacity is found from the formula

$$C = \frac{T \times W \times S}{1728}$$

Where C = capacity of roll in cubic feet per minute (in the case of limestone 1 cubic foot = 100 pounds), T = spread, W = width of roll faces in inches and S = peripheral speed in inches per minute. The above gives the theoretical capacity but on account of irregularity in feed, etc., the result should be divided by 4 for the actual capacity.

CHAPTER X

GRINDING MACHINERY

The Ball Mill

The ball mill[1] is of European origin and was used for grinding Portland cement in Germany before its introduction into this

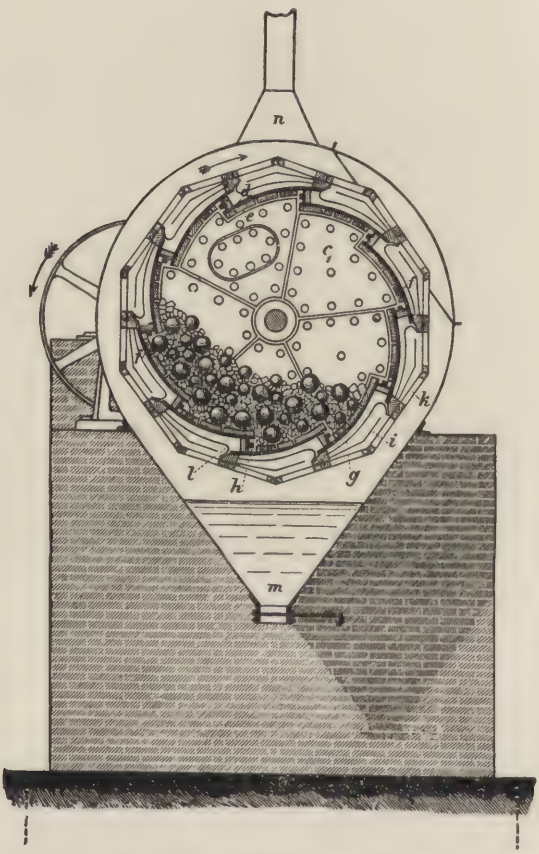


Fig. 46.—Ball mill, section showing grinding plates and sieves.

[1] F. L. Smidth & Company, New York, N. Y.; Allis-Chalmers Mfg. Company, Milwaukee, Wis.

country. It is used in connection with a pulverizing mill to prepare the material for the latter, the ball mill reducing it to a coarse grit and the pulverizer completing the operation. Ball mills have now been largely replaced in the newer plants by either

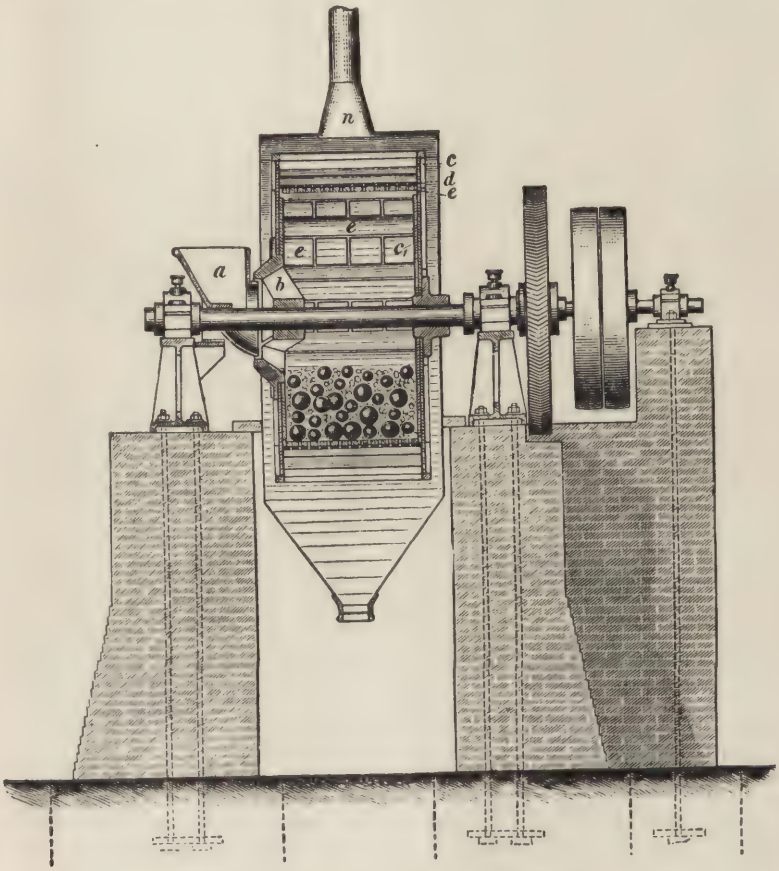


Fig. 47.—Ball mill, section through the shaft.

Hercules mills or Compeb mills, as these are considerably more efficient, but ball mills are still much employed in Europe and many of the older works in this country are equipped with them.

Figs. 46 and 47 show the construction of a ball mill. It consists of a drum containing a ton or more of steel balls. The drum is lined first with steel or chilled iron plates, (*d*) which lap one over the other to form steps. As the drum revolves, the balls drop over the steps pounding the material to pieces. The partially ground material then drops through holes in the plates on to perforated steel screens (*g*) bolted around the entire circumference of the drum. These screens retain the very coarse particles and return them to the inside of the drum. The finer ones drop on another set of screens (*l*) made of woven wire cloth, and these separate the fully ground material from the coarse and return the latter back to the mill.

The fully ground material falls into the dust-proof casing, which entirely surrounds the mill, and then down to the conveyor running underneath the latter.

When the ball mill is used to prepare material for a Fuller-Lehigh or a Griffin mill, no screens are used and the material when reduced sufficiently, about ¾ inch in diameter and under, falls through the perforations in the grinding plates directly into the casing. When used in connection with a tube mill, however, the two sets of screens are always necessary.

The ends of the drum are formed by circular plates. In the Gates and Krupp forms of this mill and also in the smaller size of the Smidth mill these plates have rigidly attached to their centers, hubs which are mounted on to a heavy shaft which revolves in dust-proof bearings. One of the hubs is provided with openings through which the material to be ground is fed. In the large size Smidth mills the shaft is omitted and the hub rests on roller bearings giving a full circular opening which will admit of the passage of lumps 10 inches in diameter into the mill. The feeding device of the Smidth mills consists of a circular revolving table provided with a scraper. The material to be ground is brought down upon the table by a spout which stops short a few inches from the former. As the table revolves the material flows out of the spout upon it and as it comes around to the scraper is brushed off into the hopper of the mill. The feed can

be regulated by adjusting the scraper so as to brush off a greater surface of the table. The Gates ball mill has a swinging feeder.

The size of the product of the ball mill is regulated entirely by the fineness of the finishing screens. Those on mills intended to grind raw material are usually 16- to 18-mesh and those on mills for clinker from 18- to 20-mesh. It is economy to so balance the screens as to get the most out of the tube mill. However, the ball mill requires much less power than the tube mill and consequently up to a certain point should be made to do all the work it will. The screens of the ball mill are apt to leak occasionally, both from wear and also from the dropping out of a rivet or bolt. A good check upon this is to run sieve tests of the product upon a No. 20 sieve once or twice a day and any abnormal weight of residue should be followed by an examination of the screens for leaks. It is necessary to brush the screens off occasionally with a wire brush as they clog with use.

All of the interior parts of the mill are of course subject to wear. The "liners" or plates which form the steps of the mill are usually made of armor-plate, manganese steel, chilled iron, etc. The latter have only the wearing surface chilled and a backing of soft gray iron to prevent cracking from the impact of the balls. The balls themselves are usually of forged steel and 5 inches in diameter. They gradually wear down, however, until the charge in the mill represents all sizes from 5 inches down to an inch in diameter. Often these small balls are perfectly round. A set of liners usually lasts from one to two years depending on their quality. When equipped with fine screens (16-mesh) and used for granulating clinker the wear on the balls amounts to about 1 pound per 20 to 30 barrels of cement ground or about ½ cent per barrel.

With all ball mills, a stack should be connected to the upper part of the casing to carry off the dust and steam. This stack may be carried out of the building, but in any event should be carried up high enough to secure a good draft and carry away all of the steam formed in the mill, by the frictional heat of the latter acting on the moisture in the material ground. If the

steam is not carried off the screens will clog up. At one time considerable attention was paid to the dust also carried away, in the belief that it represented a considerable loss. At one plant with which the writer was connected, a dust collector was installed and an effort made to save the dust. This latter was found to not only be inconsiderable in amount but also devoid of cementing properties and proved upon analysis to be practically fully hydrated cement.

One objection to the ball mill is the fact that the screening area is too small, and efforts have been made to get around this by modifying the mill in various ways. The Kominuter which is described next is such a modification. Outside screens have also been tried but never adopted to any extent. At the plant of the Riverside Portland Cement Co., Riverside, Cal., a combination of ball mills and Newaygo Separators was tried, the ball mills being screenless and the separators located just below them.

A No. 8 bill mill, the size ball mill frequently installed in cement plants, usually requires from 40 to 50 horsepower and turns out from 4 to 6 tons of raw material and from 30 to 40 barrels of clinker per hour (depending, of course, on the fineness of the screens) when used in connection with a tube mill. The balls run in sizes from 3 to 5 inches in diameter and the charge of balls for a mill of the above size weighs usually about 2½ tons. As stated above, if the ball mill is used to prepare material for a Fuller-Lehigh Mill or a Griffin Mill, no screens are required and the machine then has a capacity of from 15 to 20 tons per hour without in any way increasing the power required to operate the machine.

The repairs on a ball mill are fairly heavy, particularly when new liners are included in these. Generally they consist of bolts which drop out and screens which must be replaced because of wear. The repairs, including wear on balls and liners, amount to about 1½ to 3 cents per barrel on clinker and about 1 cent per barrel on raw material. When used without screens

for preparing material for the Fuller and Griffin mills the cost is only a fraction of this, however.

Fig. 48 gives an idea of an installation of ball mills in a modern Portland cement plant. As will be seen the mills are placed

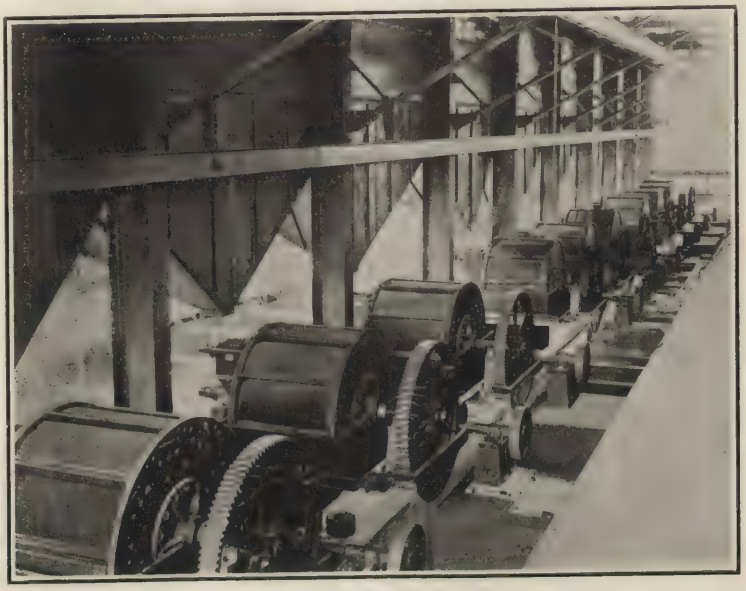


Fig. 48.—Installation of Ball Mills in a Cement Plant.

between massive concrete piers, and are arranged side by side so that all may discharge into the same screw conveyor. The stock boxes, containing the material to be ground, are just above the feed end of the mill.

The Kominuter

A modification of the ball mill which has been introduced by Messrs. F. L. Smidth & Co. is the Kominuter. This form of mill is intended to do the work of the ball mill and is now installed by this firm in place of ball mills. It consists, Fig. 49, of a drum of about the same diameter as a ball mill but of about

twice the length of the latter, suspended on a shaft supported by bearings. The Kominuter is lined just as a ball mill is with wrought iron or steel grinding plates arranged to lap and form steps. The drum is surrounded by a coarse screen tilting slightly towards the feed end, and outside of this screen, yet another

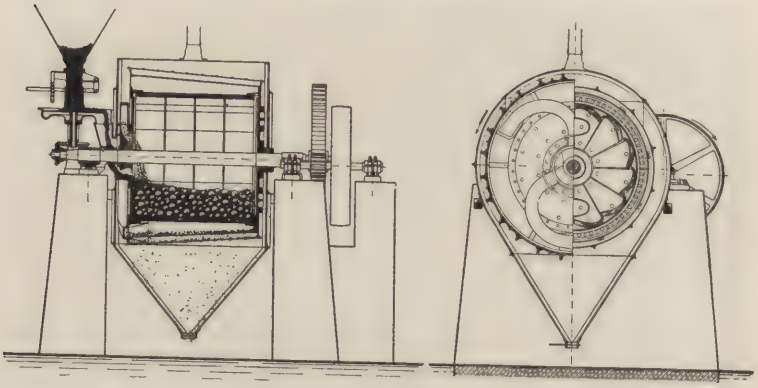


Fig. 49.—The Kominuter.

one of wire cloth. The material enters through an opening beside the shaft and is pounded to pieces by the balls. It does not fall out through the screens, however, at once, but travels through the full length of the drum and passes through openings at the opposite end, on to the first coarse screen, or perforated plate. The particles too large to pass through this are returned automatically to the interior of the mill by means of buckets and S-shaped pipes. The material passing the inside screen is caught upon the outside one of wire cloth and separated further here, the coarse material being returned to the mill as before. The feeding device has been described in the preceding section and is the same as that employed on the small Smidth ball mills.

Fig. 50 shows an installation of Kominuters at the plant of the Three Forks Portland Cement Co., Trident, Mont.

When employed for wet grinding, the Kominuter usually is provided with an outside screen known as a "Trix," the woven wire screen on the Kominuter itself being dispensed with. The

"Trix" consists of a vertical revolving screen against and through the meshes of which the partly ground slurry is thrown by centrifugal force. The fine material, as with any screening device, passes through the meshes and the coarse particles retained on them are returned to the Kominuter for further reduction. The

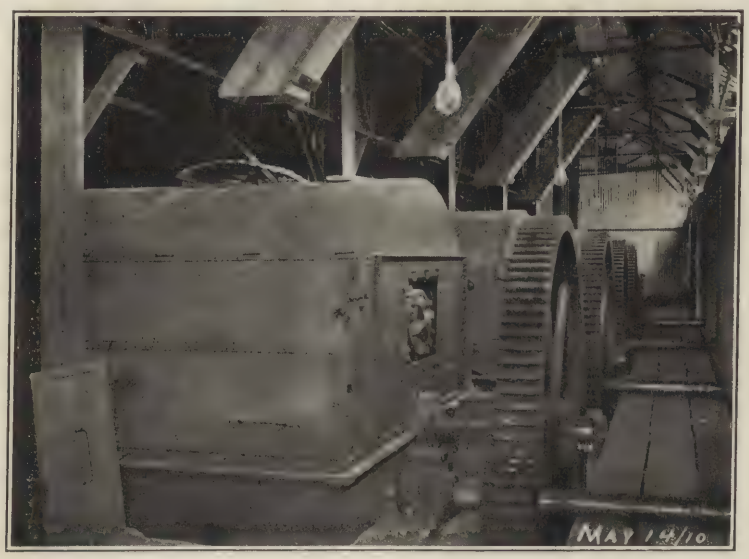


Fig. 50.—Smidth Kominuters—Three Forks Portland Cement Co., Trident, Mont.

"Trix" is usually placed above the tube mill so that the fine material can go from the screen into a small bin above the tube mill. This arrangement also permits the return of the coarse material to the Kominuter by gravity. The product of the latter is elevated to the "Trix" by means of a bucket elevator. There is usually a "Trix" installed for each Kominuter.

The Tube Mill

The tube mill as used in cement mills, Fig. 51, consists of a cylinder, 20 to 27 feet long and from 60 to 96 inches in diameter, partly filled with flint pebbles or steel balls or slugs. This cylinder is lined with some hard substances such as armor-plate,

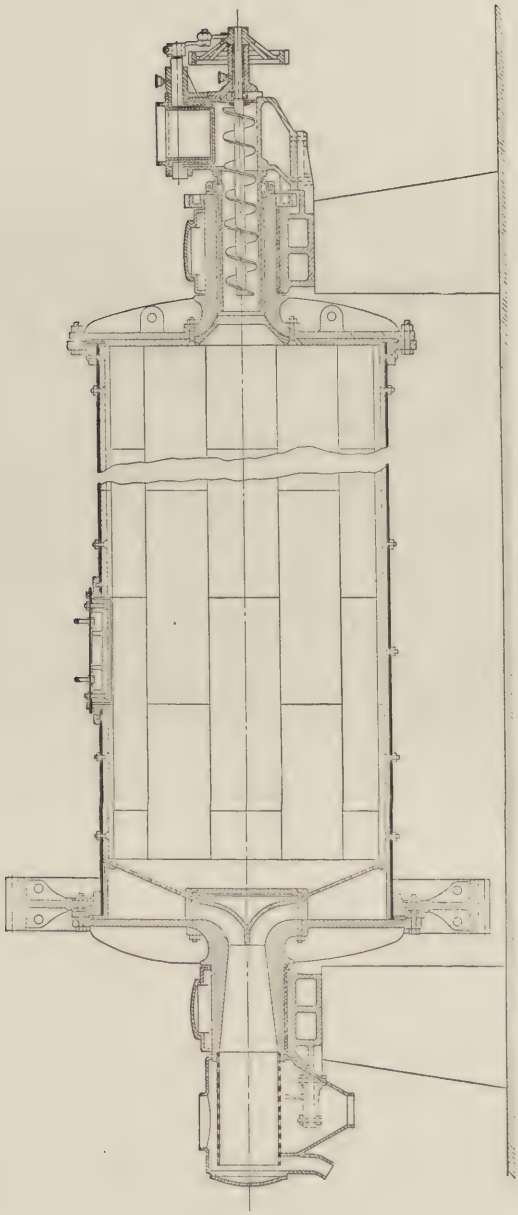


Fig. 51.—Section of standard tube mill, charge and material ground removed.

chilled-iron, quartz or trap-rock. It is revolved by means of a girth gear and pinion at one end and revolves at a speed of from 20 to 27 revolutions per minute. The material is fed in through a hollow shaft and leaves either in the same manner at the opposite end or else through a grating at the perimeter of the end.

The material is usually fed into the tube mill by means of a screw conveyor operated by a step pulley which permits the cutting down of the feed, or by a roller feed with movable gates, or by a shaker feed; any of which can be adjusted to regulate the amount of material going into the mill. The size of a tube mill is usually expressed by *the inside diameter* × *the length of shell.*

As originally introduced into the cement industry the tube mill was 5 feet to 5 feet 6 inches diameter by 20 to 22 feet long. As the cement industry grew, however, and the demand for larger outputs, both of plants and grinding machinery, with it, tube mills also began to increase in size. The newer cement plants are most of them employing tube mills 6 feet to 7 feet in diameter and the 7-foot mill may be considered as approved present American practice. Such a mill is usually made from 22 to 27 feet long. The longer mill, of course, has the greater capacity other things being equal; or, vice versa, for the same capacity will give a finer product.

A mill of this size will have its shell made of ¾-inch steel plates connected by means of outside butt-strapped joints, the straps being double-riveted and all rivets being countersunk on the inside. The heads are usually made of cast steel and in two parts, the head proper and the hollow shaft or gudgeon. The heads and gudgeons are machined so as to fit snugly and are bolted together. This form of construction allows the gudgeons to be replaced when worn. The bearings are usually made large, of the ball and socket type and are water cooled. The bearing caps are made with grease reservoirs covered with dust-proof covers. The head is usually fastened to the shell by means of an L-shaped cast iron flange-ring to which the gear-drive is also bolted.

The shell is provided with two or more man holes. These may all be on the same side or on opposite sides of the mill but if two only are used are usually placed near the ends. Metal liners are bolted to the shell, trap rock or silex block are cemented in. The lining plates should cover the entire inside surface of the mill.

The driving mechanism usually consists of a single train of cast steel cut gears. In the case of a 7 x 26 foot mill the gear should have at least 14-inch face. A 20° involute stub tooth is good practice. The pinion is usually made somewhat wider than the gear. The gear is always split rim to permit renewal and is bolted to either the head or to the L-shaped flange ring around the end of the shell. The gear may be at either end of the mill which suits the plant layout best, but generally this will be found to be the discharge end of the mill. The gear and pinion should be so arranged that they can be turned when the teeth are worn on one side. The bearings for the pinion are usually mounted on the same sole plate as the main bearings of the mill. The ratio between the gear ring and the pinion is usually about 8 to 1. This permits the mill to be driven from a slow speed motor, either by direct coupling or by a silent chain drive or belt. The mill should run so that the teeth are moving upward on the side at which the spur meshes with the tube mill gear. This is done for two reasons—first so that tools, clinker, etc., which fall into the gearing will be thrown away from the teeth and not drawn in between them, resulting in stripped gears and broken teeth; second when running in this direction the pressure is against the base and not the cap of the pinion bearing. It is, however, well to encase the gears in some form of plate metal or woven wire guard as a measure of safety to the workmen.

A new form of drive used in place of the gears is the Lenix drive. With this drive a tire of large diameter is fastened to the tube mill by means of iron rods or posts. A belt is passed around this and the small pulley on the driving shaft. The belt is made to wrap around nearly three-quarters of the surface of the latter by means of an idler, instead of gripping only a small portion of its rim, as would be the case with an ordinary belt drive between such short centers.

The feeding device is very important since the fineness of the product turned out by the tube mill, depends entirely upon the rate of feed. That is within certain limits, the less material fed into the mill the finer the product. The writer's experience has been that the product of the tube mill varies considerably in point of fineness. This is no doubt due to the fact that the feeders do not supply the material to the mill in a regular enough stream and, since the fineness of the product is controlled indirectly by the quantity of material fed to the mill, it follows that there is considerable variation in fineness if the feed is irregular. Samples taken, say every half hour, from one tube mill will frequently show a variation of 10 per cent between extremes when tested on the No. 100 sieve, although the attendant may not have increased or diminished the amount of material during that time. Of course, where a number of mills are working side by side, the samples drawn from the combined product at similar intervals do not show such variations.

Rocker, roller and screw feeds have been used to advantage. Each manufacturer of tube mills has his own ideas as to these. Generally the feeder consists of two parts, a screw, rocker or roller arrangement controlled by some means whereby the frequency of rotation or the extent of oscillation may be varied as desired, and beneath this a screw operating in the hollow shaft of the mill. The former serves to regulate the amount of material fed to the mill and the latter to carry it in. The feeder is usually provided with a clutch so that the flow of material to the mill may be entirely shut off at will. Dry material is fed to a tube mill from an overhead steel bin holding material enough for several hours' run. Wet process tube mills are often provided with a scoop feed arrangement which dips the material out of a trough.

When originally introduced into this country, tube mills were lined with silex or flint blocks. Trap rock, gannister and other hard natural rocks were also used to a limited extent. The large mills of the present day, however, and many of the smaller mills now in use are lined with manganese steel, chilled white iron or some hard iron alloy such as iron containing a small amount of

copper. The flint or silex blocks formerly employed, and still used to some extent, are about 6 x 8 inches area and 3 inches thick. They are laid flat and cemented in with Portland cement.

The chilled iron liners are now made about as large as they can conveniently be handled, the exact size varying with the size of the mill in which they are to be used. For a 7 x 22 foot mill, a liner 14½ inches x 30 inches in area by 1¼ inches to 2 inches thick is often employed. Sometimes these liners have smooth faces and sometimes they have ribs running parallel with the axis of the mill, the idea of the latter being to tumble the charge over to a greater extent. It is doubtful if there is any advantage in the ribbed liner over the smooth-faced one. The metal liners are bolted to the shell and feed-end of the mill, the bolt heads being countersunk into the liner and the nuts on the outside of the shell. Liners of hard rubber have recently been proposed.

The discharge end of the mill is usually provided with a grid or screen. This is of many types. The most usual one, however, is a slotted screen made of manganese steel and in the form shown in Fig. 52. The slots of this are usually about ¼ inch wide on the side next the grinding medium and ⅜ inch on the outside or discharge side. This tapering is to prevent wedg-

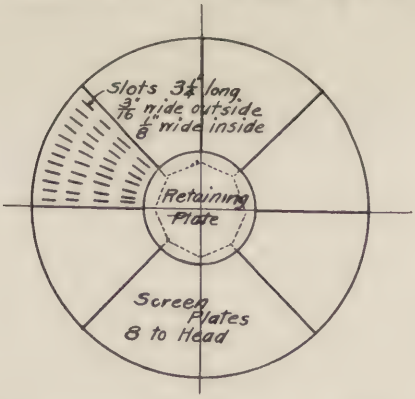


Fig. 52.—Slotted diaphragm tube mill discharge head.

ing of the balls or slugs in the slots, the idea being that any of the former small enough to enter the slots will pass through these because of the increasing width.

The fine material passing through the grating is conveyed to the gudgeons by means of lifting plates cast on the inside of the discharge head. The discharge gudgeon is provided with a slotted metal screen for removing broken pebbles, slugs or balls from the product. The ground material passes through the screen into a dust-proof casing around this and thence to the conveyor, etc.

An improved form of bar screen is shown in Fig. 53. This was devised by the Traylor Engineering & Manufacturing Co., Allentown, Pa. It is made of drop forged tool steel bars, the

Fig. 53.—Discharge head screen made of tool steel bars—Traylor Engineering and Manufacturing Co.

openings between the bars being $^3/_{32}$ inch. The bars are made interchangeable and are held in place by means of hard steel lining plates. The convex shape of the head is designed to promote the passage of the material through the screen.

In the Smidth tube mill the discharge is at the perimeter instead of through the gudgeon at one end. In this mill, the screen

is usually arranged as shown in Fig. 54. The screen is usually made of bars and the end is surrounded by a dust casing of steel or wood.

The first tube mills were charged with flint pebbles. These are imported from France and Denmark, although one or two of the

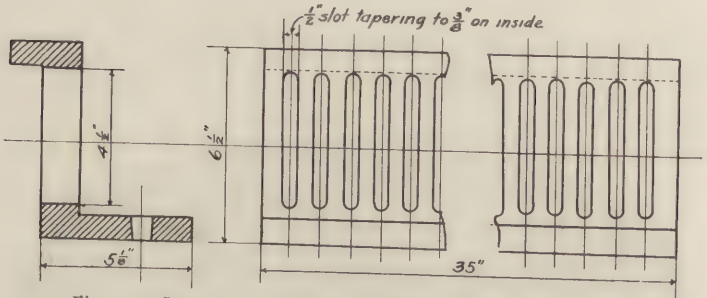


Fig. 54.—Screen for use with peripheral discharge tube mill.

Western plants have found local pebbles which give them good satisfaction. Generally, the American product proves too soft and breaks up in the mill. A good pebble should stand a considerable blow with a hammer, without breaking, and, in the mill, should wear down and not break up. Except in starting up a mill, no small pebbles are used and those fed in are oval-shaped and about 3 x 2 inches. Crushed trap-rock has been tried a number of times in place of pebbles, but results obtained do not seem to warrant general adoption of this material at any plant. The mill is usually filled with pebbles to slightly above the center line. As those pebbles above the line balance a corresponding weight of those below, an extra weight of pebbles is obtained without increasing the power required to turn the mill, over the older way of not quite half filling the mill. This extra load of pebbles, provided it is not carried too far, materially increases the output of the mill.

About ten years ago, a number of plants began to replace about a fifth of the pebbles in the tube mill with small metal slugs or balls. These slugs were made of some hard material such as chilled iron or alloy steel. The tube mill was provided with a perforated diaphragm about 4 feet from the discharge end and the compartment so formed was filled half full of the slugs. This end of the mill was lined with chilled iron plates.

The addition of the slugs increased the output of the mill at least 33⅓ per cent but of course also increased the power required to operate the mill by about 25 per cent. The addition of the slugs therefore increased the output per horsepower-hour also.

Following the employment of metal in a compartment it soon became the general practice to charge the entire mill with some form of metal grinding media and now pebbles are seldom employed. The output of the mill as has been said is very much greater where a metal charge is used, the power and repairs are not increased thereby. The increase is shown by Tables XVIII and XIX. It has been found that the output of the tube mill depends on the weight of the charge.

The following example[1] illustrates this, the mill in question being a 5 foot 6 inch x 22 foot, central discharge, tube mill.

Charged with 24,000 pounds flint pebbles, output 20 barrels, power 95 horsepower.

Charged with 18,000 pounds flint pebbles and 11,000 pounds steel balls, output 26 barrels, power 120 horsepower.

Charged with 24,000 pounds steel balls, output 28 barrels, power 134 horsepower.

Charged with 30,000 pounds steel balls, output 35 barrels, power 185 horsepower.

Charged with 36,000 pounds steel balls, output 40 barrels, power 220 horsepower.

Metal having a much higher specific gravity than a rock the weight brought to bear on the material being ground is much greater when metal is employed than when pebbles are used and hence the crushing force is much higher. Also the slugs or balls

[1] Communicated to author by L. C. Hawk, chemist, Dexter Portland Cement Co.

are much smaller than pebbles and hence the grinding surface is much greater. For example, a three-inch sphere of flint weighs 1.32 pounds and has a surface area of 28.3 square inches. The same volume of cast iron in 1-inch balls weights 3.91 pounds and has a surface area of 43.0 square inches. In substituting 1-inch iron balls for 3-inch flint pebbles, therefore, we have increased the weight in a given volume of charge by about 200 per cent and the surface area by about 50 per cent.

The slugs or balls wear at the rate of from 0.05 to 0.075 pounds per barrel of cement ground, depending of course on the hardness of the slugs themselves and the clinker.

A number of patented forms of metal slugs and balls have been introduced such as "cylpebs" (F. L. Smidth & Co.) and "concavex" (Allis-Chalmers Mfg. Co.). It is doubtful, however, if the form of the media has much effect on the efficiency or output of a tube mill. In the writer's opinion the main requirements are hardness and toughness or a slug or ball which will wear well and which will not crack up in the mill.

The use of a metal charge in place of pebbles not only increases the output but also increases the finer particles in cement. That is to say, in two samples of cement, one ground in a mill equipped with slugs and the other in one without, the slug ground cement will be found to test the finer on the No. 200 sieve. This is shown by the results given below. The results show the fineness obtained without slugs and with them, at the same mill.

Comparison of Cement Ground With and Without Slugs

	Passing No. 100 sieve	Passing No. 200 sieve
With	92.9	80.7
Without	92.9	74.1
With	94.4	83.0
Without	94.4	76.4
With	95.8	96.3
Without	96.0	79.5
With	97.0	87.8
Without	97.0	81.9

The fineness of the product, output, etc., of the tube mill depend, as has been said, on the amount of material fed to the mill. Since there are no fine screens on the mill it follows that the material will pass through the mill at the same rate at which it is being fed into it. The more rapidly the material passes through, the less time it will remain in the mill and hence the less opportunity it will present for grinding. The method of regulating the fineness of the product from the mill is, therefore, by regulating the quantity of material fed to the mill in a given time. To increase the degree of fineness of the product, other things being equal, the output of the tube mill must be reduced. Similarly if the material is ground too fine the output is increased, etc. The condition of the material fed to the tube mill also has a great bearing on the output. This mill is essentially a pulverizer and does not handle coarse material efficiently. Generally speaking, best results are obtained when the material fed to the tube mill will all pass a 20-mesh test sieve.

It has also been found that while a tube mill will grind slurry it will not grind damp materials advantageously. In the dry process, therefore, the raw materials should be reduced to not more than 1 per cent moisture before grinding. In the wet process, on the other hand, there must be sufficient water to form with the material a mixture which will flow through the mill—the amount approximating 50 per cent of the solids by weight.

As showing the progress of grinding in a tube mill Fig. 55 will be found interesting. A 5½ x 22-foot tube mill was shut down, the man-hole taken off and samples drawn every 4 feet from the feed end of the mill. These samples were tested for fineness and the results plotted to curves as shown in the diagram.

Owing to their length, a battery of tube mills is a difficult proposition to drive directly from one line shaft and considerable power is often wasted in counter-shafts. The employment of bevel gears would perhaps simplify the arrangement as it would allow the mills to be placed side by side and the line shaft to be run at right angles to the mills. The bevel gears, however, are unsatisfactory and in spite of the simplifying of the arrange-

ment of the mills, are not employed. Motor drives allow an ideal arrangement of the mills, side by side, which cannot be done without counter-shafting where more than two or three mills are driven from the same line shaft. Most cement plants are now motor driven—all the newer ones are—and this has very much simplified the problem of driving a battery of tube mills.

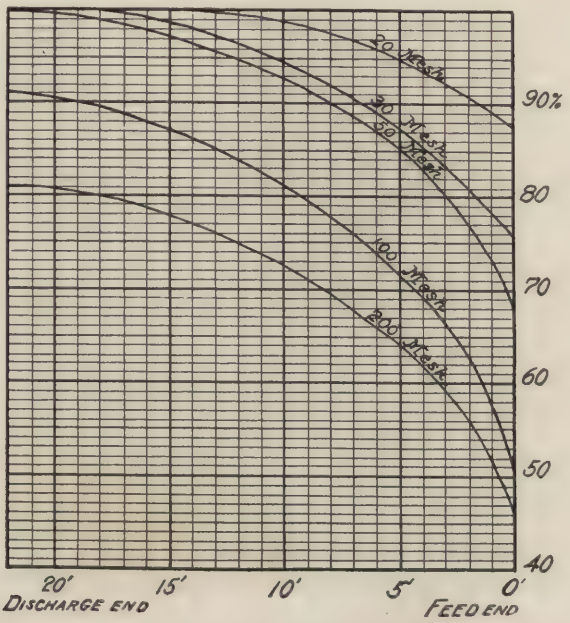


Fig. 55.—Cement fineness determinations in a 5 ft. tube mill.

At first, the connection between the motor and pinion shaft was by means of leather belting, then silent chain drives were used. Now the pinion shaft is direct connected to synchronous motors. A magnetic clutch is usually employed between the motor and the pinion to aid in starting. The General Electric Co., however, have perfected a super-synchronous motor which can be used without the magnetic clutch and the Westinghouse Electric Mfg. Co. have combined the clutch with the motor towards the same end. All the more recent installations of tube mills are driven

by means of synchronous motors. This not only makes a compact layout and does away with belts and chains, but the employment of the synchronous motor here helps raise the power factor of the plant—an important thing in any event and particularly so where power is purchased.

The output, power required to operate, etc., of tube mills depend on many things, as has been indicated above, such as the coarseness and moisture in the feed, the toughness of the material to be ground and weight, nature, condition, etc., of the grinding charge. Tables XVIII and XIX will, however, indicate what may be expected under average conditions, where the feed will pass a No. 20-mesh screen and the output is ground to a fineness of 80 per cent passing a 200-mesh sieve.

TABLE XVIII.—Data on Tube Mills Charged with Flint Pebbles.

Tube mills lined with Silex bricks, 2½ inches thick.

Fed with 20-mesh material of average hardness and grinding to 80 per cent passing the No. 200 sieve.

Size of mill	H. P. to start	H. P. to operate	Capacity per hour—Raw material—Tons	Raw material—Bbls.*	Clinker Bbls.	R. P. M. of mill	Initial charge of pebbles† lbs.
5′0″ x 22′	120	75	5	16	15	27	20,000
5′6″ x 22′	150	95	6½	20	20	26	24,000
6′0″ x 22′	185	115	8	25	24	24	29,000
6′6″ x 22′	220	140	9¾	31	28	22	34,000
7′0″ x 22′	250	160	12	38	34	20	39,000

*Raw material equivalent to one barrel of cement. Taken as 630 pounds.
†Capacity and power to operate depend largely on weight of charge.

TABLE XIX.—Data of Tube Mills Charged with Steel Balls, Slugs, Etc.

Tube mill lined with 1½ inch chilled iron plates. Charged with ⅞ inch balls. Fed with 20-mesh material and grinding to 80 per cent passing the No. 200 sieve.

Size of mill	H. P. to start	H. P. to operate	Capacity per hour—Raw material—Tons	Raw material—Bbls.*	Clinker Bbls.	R. P. M. of mill	Initial charge of balls† lbs.
5′0″ x 22′	305	195	16	50	49	27	33,000
5′6″ x 22′	385	245	20	72	61	26	41,000
6′0″ x 22′	455	290	24	75	73	24	49,000
6′6″ x 22′	550	350	29	90	87	22	58,000
7′0″ x 22′	625	400	33	105	100	20	67,000

*Raw material equivalent to one barrel of cement. Taken as 630 pounds.
†Capacity and power to operate depend largely on weight of charge.

Ball-Tube Mill, Hardinge Mill, Rod Mill, Etc.

Efforts have been made to substitute for a ball mill a tube mill in which the lining was made of chilled iron and corrugated slightly, the pebbles being replaced by steel balls, the idea being to do away with the screens of the ball mill, always a source of trouble. Such a mill under the name "Ball-tube Mill" has found a limited use as a preparatory mill for the tube mill. This latter type of pulverizer, however, does not pulverize coarse material very readily and requires a very regular and not too coarse feed, the very large pieces usually working their way entirely through the mill without being reduced much in size. Hence the ball-tube mill alone has not found very general use. Fig. 56 shows the ball-tube mill made by the Chalmers & Williams Co.

These ball-tube mills are usually installed in connection with some form of outside screen such as a "Newaygo" or Tyler "Hummer" (Page 236), the screens being placed on top of the bins feeding the tube mill, as in this position the fines can be dis-

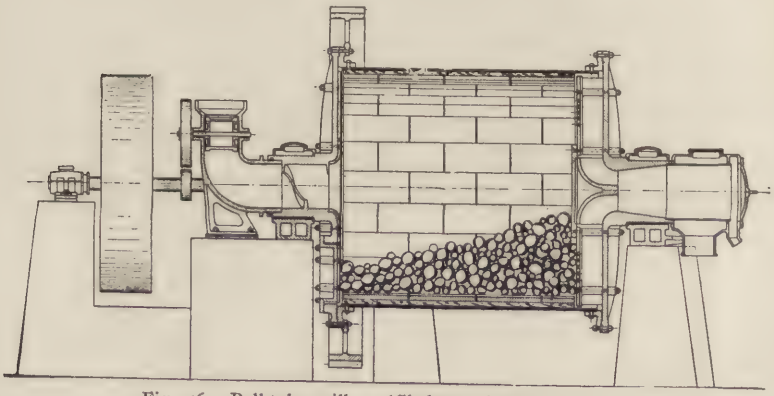


Fig. 56.—Ball-tube mill. (Chalmers & Williams Co.)

charged directly into the feed bin and the coarse material led back to the ball-tube mill.

Ball-tube mills are economical as regards both power and repairs. In connection with some form of hammer mill to prepare material for them they should give excellent service. The

objection to them is the need of employing an outside screen. On the other hand, if a screen must be used, as with most granulators, there is an advantage in having this where it may be easily gotten at for repairs. The installation is not so compact as where Hercules or Compeb mills are used.

A 6 ft. diam. x 6 ft. long ball-tube mill grinding from 2 inch to 20-mesh will have a capacity of from 30 to 40 barrels of clinker per hour and will require about 100 horsepower to operate. Such a mill will operate at about 24 revolutions per minute and have a charge of 7 tons of assorted balls, the maximum ball used being 4 inches in diameter.

A mill of somewhat similar type is the Hardinge or "Conical" ball mill.[1] This is much used in mining, but has never come into use to any extent in the cement industry. This mill differs from the ball-tube mill chiefly in its shape, which will be evident by reference to Fig. 57. The idea of the cone shape is that, em-

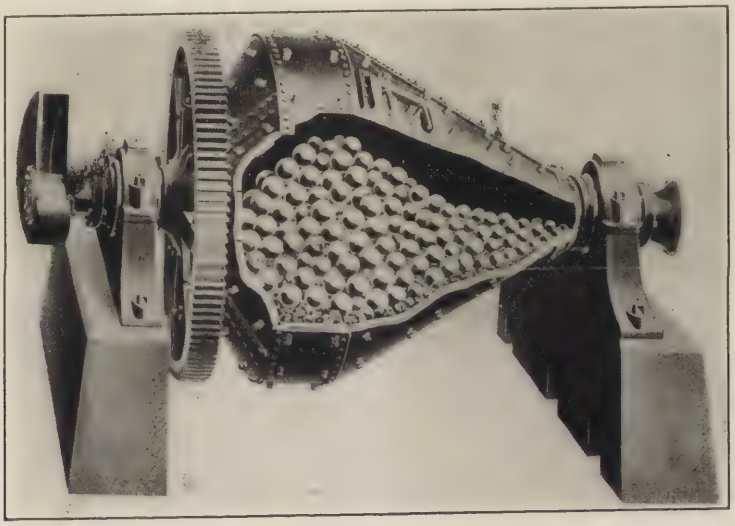


Fig. 57.—Hardinge "conical" ball mill.

ploying balls of assorted sizes, the largest balls will segregate in that portion of the mill where the cone is largest, the smallest

[1] Hardinge Mill Company, New York, N. Y.

balls where this is smallest, etc. As the largest diameter is at the feed end, the largest balls act on the coarsest material, etc. As installed in cement plants, these mills usually employ an outside screen. The manufacturers of this type of mill are at this writing (1925) advertising an "air swept" mill, in which a current of air is passed through the mill by a blower. This carries the fines out of the mill and into a cyclone collector, where the fines settle and drop into a conveyor as with the Raymond roller mill. An 8 foot diameter x 36 inch Hardinge mill will grind from 40 to 60 barrels of cement to 20-mesh and requires about 140 horsepower to operate.

Still another mill of this type is the Marcy or "Rod Mill" in which steel rods take the place of balls. These are the full length of the mill and to permit replacing these in the mill, the discharge end is hinged.

Compound Mills

Efforts have been made at various times to combine the ball and tube mill in one machine, or rather to divide the tube mill into two or more compartments each of which was supposed to grind material of a different degree of fineness. In one of the earlier types of tube mills there were three 7 foot compartments. These were charged with pebbles of varying sizes, the largest being in the first compartment (feed end) and the smallest in the last. The large pebbles were supposed to grind the coarsest material and the small pebbles the almost fully ground material, etc. The difficulty with this mill was to keep open the slots or perforations in the diaphragms separating the compartments.

In a German type of mill ("Löhnert's Compound Mill"), both ball and tube mills are combined in one. The feed end of the cylinder is larger in diameter than the main portion and is provided with a step lining, this compartment which contains the steel balls being separated from the rest of the mill by means of a diaphragm. The discharge end of the mill is filled with pebbles. The material is first granulated in the upper part and then pulverized in the lower.

Compeb Mill

The "Compeb" mill[1] is a combination ball and tube mill designed to take clinker as received from the kilns or raw materials as crushed by a hammer mill or crushing rolls. The mill is suitable for either wet or dry grinding. The Compeb mill is made in several sizes. Those designed for cement mill work are 7 feet in diameter and from 22 to 26 feet long. Figure 58 shows the mill equipped for dry grinding and Fig. 59 the wet Compeb mill. As will be seen by reference to the first of these illustrations, the Compeb mill for dry grinding is constructed quite similarly to a tube mill except for the division head. The mill consists of a steel tube lined with chilled iron ribbed plates and driven by a girt gear. This shell is, however, divided into two compartments, the division line of which is about 5 feet 6 inches from the feed end. The first compartment of the 26-foot mill is filled with 22,000 pounds of forged steel balls and the second compartment with 74,000 pounds of "concavex." (See page 206). The coarse grinding is done in the first compartment with the large balls and the pulverizing in the second with the concavex. The most distinctive feature of the Compeb mill consists of the division head employed to separate the two compartments, the construction of which can be noted from Fig. 58. This consists of a peripheral discharge screen, *a*. This is made of tool steel grid bars machined so that when they are laid side by side they form a grid screen with accurate spacings. These bars are supported on a grid frame, *b*, and are held in place by a manganese steel wearing plate or head, *c*, at one end and a keeper ring, *d*, of the same metal at the other. A second manganese steel wearing plate, *e*, is at the upper end of the discharge compartment, and the two wearing plates, *c* and *e*, are held in place and also separated by a heavy steel spider, *f*. This arrangement leaves a space between the two plates. The plate *c* is solid but the plate *f* has an opening *g* at the center.

The material to be ground enters the mill at *h*, being fed in by an automatic rocker feeder, *i*, and, entering the compartment

[1] Allis-Chalmers Mfg. Company, Milwaukee, Wis.

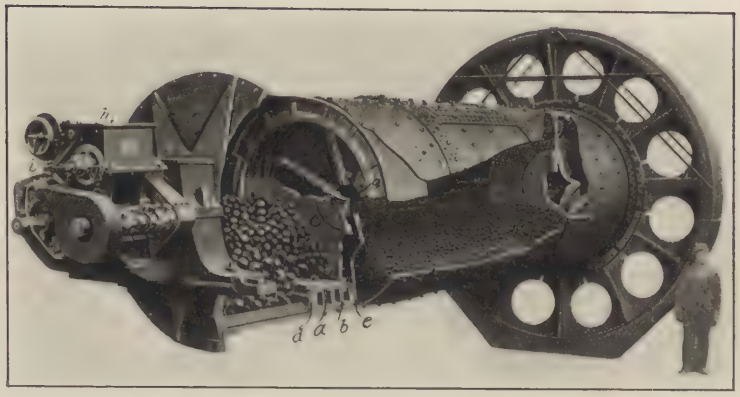


Fig. 58.—Compeb-mill equipped for dry grinding—Allis-Chalmers Mfg. Co.

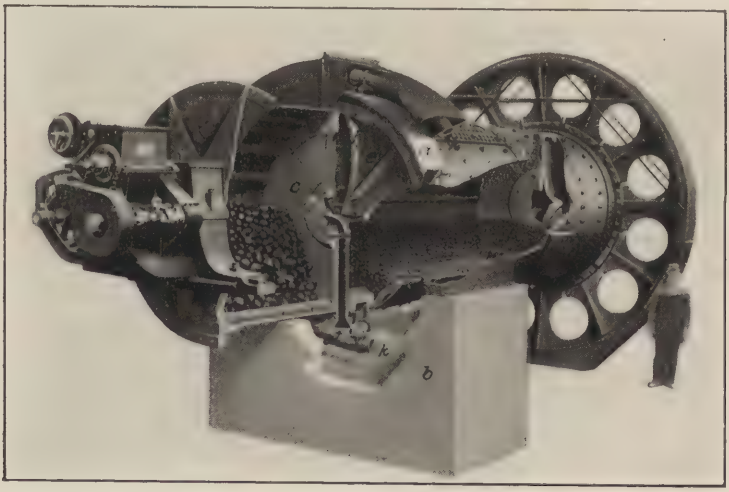


Fig. 59.—Compeb-mill, equipped for wet grinding—Allis-Chalmers Mfg. Co.

with the balls, is ground by these down to wheat size, when it passes through the grid screen. The vanes of the grid frame, *b*, are made in the form of a worm or helix and pass the ground material into the compartment between the wearing plates, *c* and *e*. The spider, *f*, is provided with lifting vanes which carry the material up and through the opening in the center of the plate *e* and so into the concavex compartment. Here, the final work of pulverizing is done. The finely ground material works its way out through a screen head, *k*, and a hollow trunnion at the discharge end, just as with the tube mill.

The Compeb mill as outlined above can be employed for wet grinding, but in the newer mills the design of the division head has been modified as shown in Figure 59. Here the plate, *c*, at the discharge end of the ball compartment is a slotted screen. The material passing this flows down between the two plates, *c* and *e*, and on to a woven wire screen, *a*, attached to a housing fastened to the shell of the mill. Material of the desired size passes the screen, *a*, and falls into the concrete trough, *b*, while the coarse material retained by the screen is returned to the ball compartment at *g* by means of the spider vanes, *f*. The fine material is picked up out of the trough, *b*, by means of the two scoops, *k*, located diametrically opposite each other, and fed into the concavex compartment.

The Compeb mill can be driven by any appropriate means but a synchronous motor and magnetic clutch, as described for tube mills, are usually employed.

The Compeb mill as installed in cement mills is made in three sizes as follows:

Mfg's. No.	Diameter of shell	Length of shell	Charge of balls	Charge of concavex
722	7 ft.	22 ft.	22,000 lbs.	60,000 lbs.
724	7 ft.	24 ft.	22,000 lbs.	67,000 lbs.
726	7 ft.	26 ft.	22,000 lbs.	74,000 lbs.

A No. 726 Compeb mill will grind from 50 to 75 barrels of cement and from 20 to 25 tons of raw material. The mill requires about 450 horsepower and is usually operated by a 480 to 500-horsepower motor.

Griffin Mill

The Griffin mill,[1] shown in Figs. 60 and 61, has now been superceded to some extent by the Hercules mill, a later model

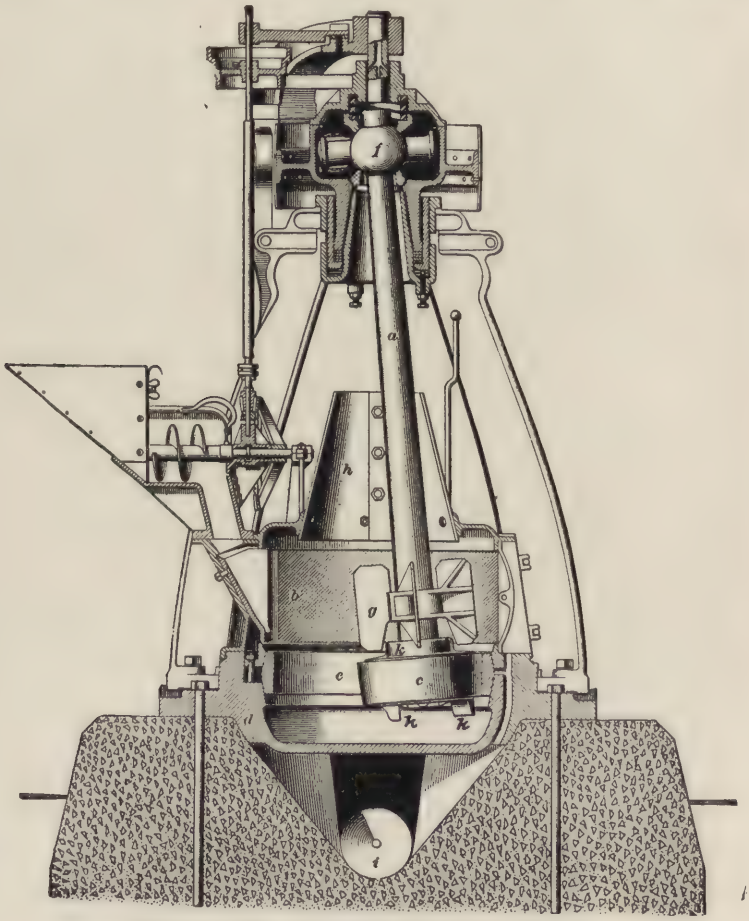


Fig. 60.—Griffin mill (Bradley Pulverizer Company).

of this. Many of the older cement mills, however, still employ Griffin mills. Referring to Fig. 60, which represents a 30-inch

[1] Bradley Pulverizer Company, Allentown, Pa.

mill of the old type, it will be seen that it consists of a steel die or ring, *e*, against which a roll, *c*, also of steel is made to revolve, and it is between the face of these two that the material is ground. The roll is suspended by a shaft, *a*, from a spider, *d*, and is actuated by a pulley, *e*, to which the shaft is attached by a universal joint, *f*. The fully ground material is sucked up and forced through screens, *b*, by fans, *g*, attached to the shaft and the coarse particles falling back into the pan, *d*, of the mill are drawn between the fan and the die by means of plows, *k*, attached to and below the roll. The finished product passes through the screens and downward between these and the outer casing, through openings in the base to the screw conveyor, *i*, located below the mill.

The roll is revolved within the die in the same direction that the shaft is driven, but when coming in contact with the die it travels around the die in the opposite direction from that in which the roll is revolving with the shaft. The roll is pressed out against the die by centrifugal force, the amount of this, of course, depending on the weight of the roll and the speed at which the shaft revolves. This mill is made in three sizes:—*viz.*, with 30, 36 and 40 inch dies. Formerly the 30-inch mill was used in the cement industry. Subsequently the 40-inch mill was introduced.

The fineness is controlled by the size screen employed and also by the amount of material fed to the mill.

The Griffin mill is usually driven from either a line shaft by means of a quarter turn belt or a vertical motor.

The principal parts subject to wear are the die and roll. The shafts also frequently break and the screens as we have said get torn. Repairs on raw material generally run from 2 to 3½ cents per ton and on clinker from 1½ to 2½ cents per barrel. Both manganese steel and chilled iron rolls and dies are employed. The breaking of the shafts constitutes an item in the cost of keeping these mills in repair. The 40-inch mill has a frame built up of angle irons, in order to lessen the shock on the shaft and so decrease the breaks, as such a frame is more elastic than one made of cast iron. The die usually wears most at the center and becomes concave, when this occurs the upper and lower edges

of the roll are liable to come in contact with the bare metal of the die, causing portions of the roll to be broken off. This is avoided in some plants by removing the dies when they become worn and turning them even on a lathe.

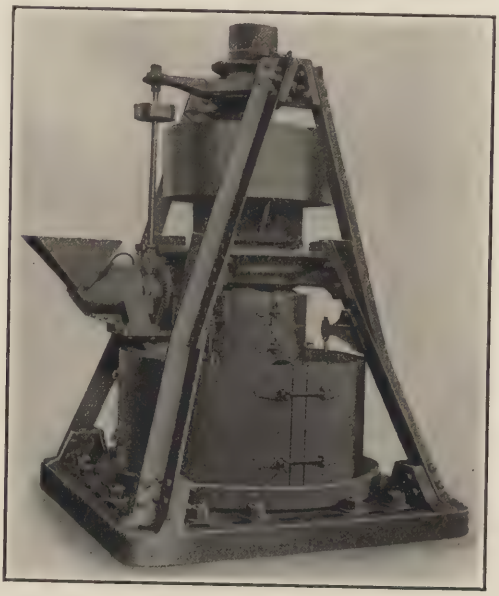


Fig. 35.—The Griffin Mill (side view)

A 30-inch Griffin mill takes ½ inch material, requires about 25 to 30 horsepower and gives an output of from 1½ to 2 tons of raw material when grinding to a fineness of 92 per cent through the No. 100 sieve and 4 to 6 barrels of clinker with an expenditure of from 30 to 35 horsepower grinding to the same degree of fineness. The 40-inch Griffin mill takes ¾ inch feed, will grind from 12 to 15 barrels of clinker or 4 to 6 tons of hard raw material, 80 per cent passing the 200-mesh sieve and requires 75 horsepower when working on soft raw materials to 85 horsepower on clinker.

About fifteen years ago, the manufacturers of the Griffin mill brought out a "Three Roll Mill" somewhat similar to the single

roll Griffin mill just described, and also to the Huntington mill mentioned further on. This mill has three rolls, in place of the one roll of the older form, which are suspended by suitable means from a single shaft, to which latter is keyed the driving pulley. The mill is provided with screens, fans and ploughs which perform the same work as in the single roll mill. This three roll mill, however, has now been greatly enlarged and improved and is known as the "Bradley Hercules" mill, which is described in the next section.

Bradley Hercules Mills

The Bradley Hercules mill[1] is shown in Figs. 62 and 63. This mill was first tried out in 1921 and has during the intervening time become quite popular in the cement industry. It is employed entirely as a preliminary mill to the tube mill. Fig. 62 illustrates the construction of the mill. Its principle of action is quite similar to that of the Griffin mill previously described. It consists of a cast iron base, *a*, and a heavy steel frame, *b*, on which latter the central shaft, *c*, and driving gears, *d*, are supported. A yoke, *e*, is keyed to this shaft and three rolls (of which one, *f*, is shown) are suspended from this yoke by means of cross arms, *g*, which work in dust-proof bearings and permit the rolls to swing out against the die *h*. The roll shaft and the cross arm are in the form of a T with the roll head at the base. The rolls are free to swing, and as the shaft is revolved they are pressed out against the die by centrifugal force. The lower end of the shaft rests in a step bearing in the base of the mill and this, as are all other bearings in this mill, is dust-tight and provided with a lubricating device. The shaft is revolved by means of a pair of bevel gears, *d*, in a dust-proof casing on top the frame. The rolls are not driven, but are free to rotate, and are revolved only by the fraction between die and roll.

The screens are placed just above the die, as with the single roll Griffin mill, and are surrounded by a dust-proof casing, *k*, The fully ground material falls out of the mill through openings, *l*, behind the die into a conical hopper in the concrete founda-

[1] Bradley Pulverizer Co., Allentown, Pa.

tion and from this in turn is discharged by gravity into a conveyor beneath the floor or into the boot of an elevator.

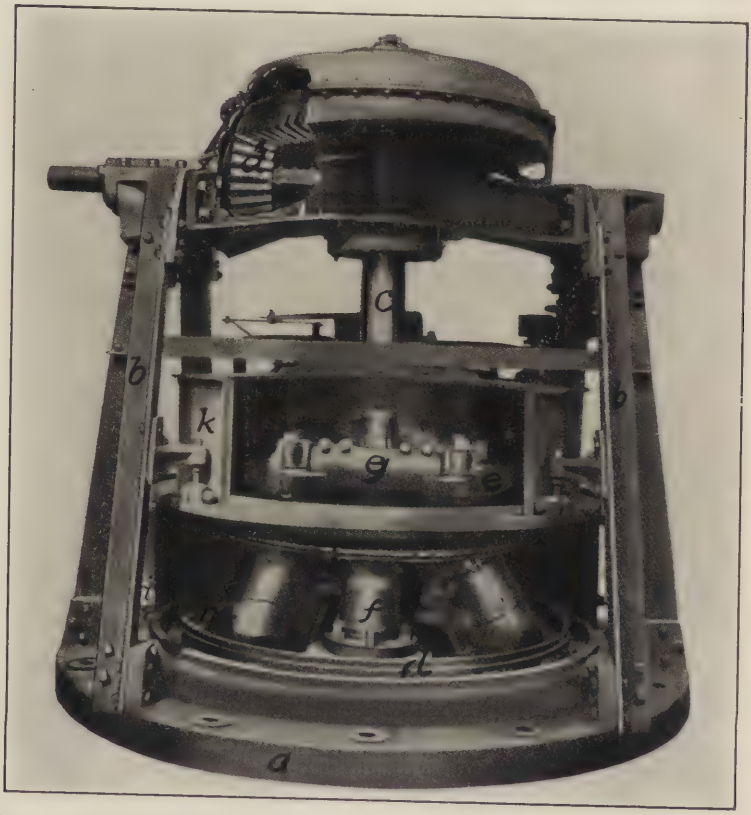


Fig. 62.—Bradley-Hercules mill, screen and cover removed, and gear casing cut away.

The material is fed into the mill from an overhead bin by means of a table feeder similar to that employed for the ball mill and is led by means of chutes so that it falls directly between the rolls and die. Plows also throw the material in the base of the mill between the rolls and die.

The rolls are 22 inches diameter and the die 66 inches internal diameter. The shaft revolves at a speed of 125 to 130 revolu-

tions per minute. Each roll weighs about 1,000 pounds and exerts a crushing effect against the die of about 13,000 pounds.

Fig. 63.—Installation of Bradley-Hercules mills—Phoenix Portland Cement Co., Birmingham, Ala.

The mill is usually driven by a 250 or 300 horsepower horizontal motor (360 to 400 revolutions per minute) direct connected through a flexible coupling to the pinion shaft. It may also be driven by belting from a line shaft or by a silent chain or belt from a motor. Induction motors of either the squirrel cage or slip ring type are commonly employed, but where power conditions in the plant are such as to make this desirable, synchronous motors may be employed to advantage, with or without a magnetic clutch as the motor may demand.

The product of the Hercules mill, if the proper screens are employed and these are kept in good condition, will practically

all of it pass a 20-mesh sieve and 50 to 60 per cent will pass a 100-mesh sieve. In order to obtain this fineness, a 6 or 8-mesh heavy wire screen is generally employed. The mill will take raw material direct from a No. 5 gyratory crusher or a large hammer mill or run of pile clinker and reduce same to the above fineness.

The Bradley Hercules mill has an output of from 125 to 175 barrels of clinker or from 25 to 40 tons of raw material per hour. The power required to operate is from 240 to 290 horsepower depending somewhat on the output and material to be ground. These mills are usually installed with an indicating wattmeter on the motor and the feed is regulated in accordance with this, so as not to overload the motor.

The base of the mill is sometimes set level with the floor and sometimes it is elevated sufficiently to allow the conveyor to be placed just below the floor. The latter arrangement does away with tunnels but necessitates a platform being built around the mill. The conveyor trough should be provided with a stack to allow proper escape for the air and steam and permit the air to circulate without back pressure through the screens of the mill.

The Bradley Hercules mill is very compact, the mill and direct connected motor used to drive this occupying a space about 11½ x 15½ feet. It is also probably the most economical mill for preparing material for a tube mill as regards both power and upkeep.

When the mill is in operation, it is continually handling only a limited amount of material at any one time. As soon as the material is reduced to the desired fineness, it is lifted out of the pulverizing zone and discharged from the machine. The power required to operate the machine is applied directly to either crushing the material or is consumed in friction between the shaft and bearings.

Huntington Mill

The Huntington mill is another mill of the impact or percussion type and is somewhat similar to the Bradley Hercules

Mill in principle of operation. So far as the writer knows it is used only by the Atlas Portland Cement Co.

The Huntington mill, Fig. 64, has rolls freely suspended on spindles from a revolving spider. The revolution causes the rolls to swing out and crush against the edge of the die ring.

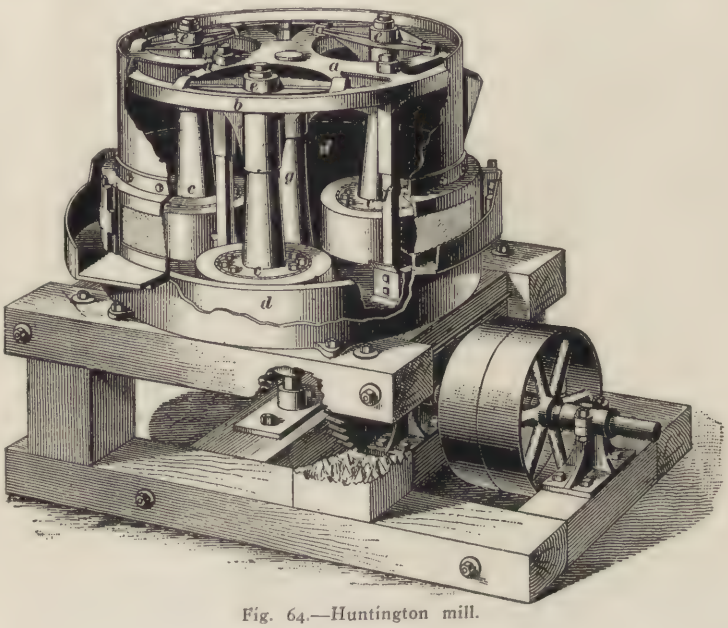


Fig. 64.—Huntington mill.

The Huntington mill is provided with fans and screens and there are four rolls. The machine generally is a great consumer of repairs and does not give a very fine product, so that it is now generally used only to prepare material for tube mills.

When so used, the Huntington mill will granulate from 12 to 18 barrels of clinker per hour. With an expenditure of 70-80 horsepower. All of the product will pass a No. 20 sieve. On raw material the mill has a capacity of from 6 to 7 tons per hour and requires 55 to 65 horsepower when furnishing a product all of which will pass the No. 20 sieve.

Raymond Roller Mill

The Raymond roller mill[1] is employed chiefly for grinding coal. It is extensively used for this purpose as it does this very efficiently. It is used to a very limited extent for grinding soft raw materials and not at all for grinding clinker. Figure 65 shows the Raymond system, consisting of mill, with separator and collector.

The Raymond roller mill consists of three parts—the mill proper, an exhauster and a collector. The pulverizing unit of

Fig. 65.—Raymond mills—Raw department of the Crescent Portland Cement Co., Wampum, Pa.

the Raymond mill consists of from two to six rolls which are freely suspended from a spider which is in turn rigidly attached to a central vertical shaft. This shaft is driven by means of a set of bevel gears from below. When the central shaft is revolved the rolls are swung outward by centrifugal force against a

[1]Raymond Bros., Impact Pulverizer Company, Chicago, Ill.

steel ring and as they are free to turn they roll around inside this ring. A plow is located ahead of each roll which throws a stream of material between the face of the roll and the ring.

The air enters the pulverizer through a series of tangential openings located around the bases of the grinding chamber and directly under the ring and rolls. That portion of material which has been reduced to a certain degree of fineness is carried up by the air current into the cone-shaped chamber above the ring. Owing to the decreased velocity of the air current here, the coarse particles fall back and are thrown up by the plows to be reground between the ring and rolls while the fully pulverized material is carried out by the air current. This air current is induced by means of an exhaust or fan.

The finely ground material is blown into a cyclone collector. This latter consists merely of a large cone-shaped chamber in which the velocity of the air is greatly decreased and consequently the particles of ground material fall to the bottom of this. The exhaust from the collector is returned to the mill through the tangential openings mentioned. An auxiliary collector is usually provided which serves as an air relief to the large collector. This is similar to the latter in all respects except that it is smaller.

These mills are subject to very nice regulation as to the fineness of the product. There are no screens in which holes are liable to wear and in consequence of this they give a product of uniform fineness. The Raymond mill also has the advantage that no elevator is required to convey this material into an overhead bin as the collectors can be set sufficiently high to allow these to discharge directly into a bin or into a screw conveyor leading to the bin, etc.

The cost of repairs at the present time will average about 2 to 3 cents per ton of coal ground. The capacity and horsepower required to operate vary with conditions such as the hardness of the coal, moisture it contains, fineness desired, etc. Table XX gives average figures when grinding dry coal to a fineness of 95 per cent passing the 100-mesh screen.

TABLE XX.—Average Capacity and Power Requirements of Raymond Roller Mills Grinding Bituminous Coal

Size mill	Capacity in tons per hour	H. P. to operate
2-Roller	2	40
3-Roller	3	55
4-Roller	4	75
5-Roller	5	85
6-Roller	6¼	100

Fuller Lehigh Mill

The Fuller Lehigh[1] mill has for its grinding elements a horizontal concave ring against the inside of which revolve four balls. These balls are propelled by four pushers attached to four equidistant arms radiating from a vertical central shaft. The material to be pulverized is fed to the mill from an overhead bin by means of a worm mounted on top of the mill. This feeder is driven direct from the mill shaft by means of a belt running on a pair of pulleys. An eccentric and link motion permits the operator to regulate the amount of material entering the mill. In addition, the feed hopper is provided with a slide so that the rate of flow of coal from the bin to the feeder can also be controlled.

The material is discharged by the feeder into the pulverizing zone of the mill and falls between the balls and the grinding ring in a uniform continuous stream and is so reduced to a fine powder.

The screen type mill, Fig. 66, is provided with two fans, one of which operates in what is known as the separating chamber or that portion above the balls and ring. The other fan operates in a housing immediately below the ring. The upper fan lifts the particles of pulverized coal from the grinding surfaces into the separating chamber where these particles are held in suspension. The separating chamber is surrounded with two screens, one an inner screen of heavy perforated sheet steel and the other an outer screen of wire cloth. The finely pulverized coal is sucked out of the separating chamber by the lower fan and passes through the screens and down into the lower fan housing from

[1] Fuller-Lehigh Company, Catasauqua, Pa.

which it is discharged through a spout. The screens do not actually screen the coal but serve to control the flow of air and so regulate the fineness.

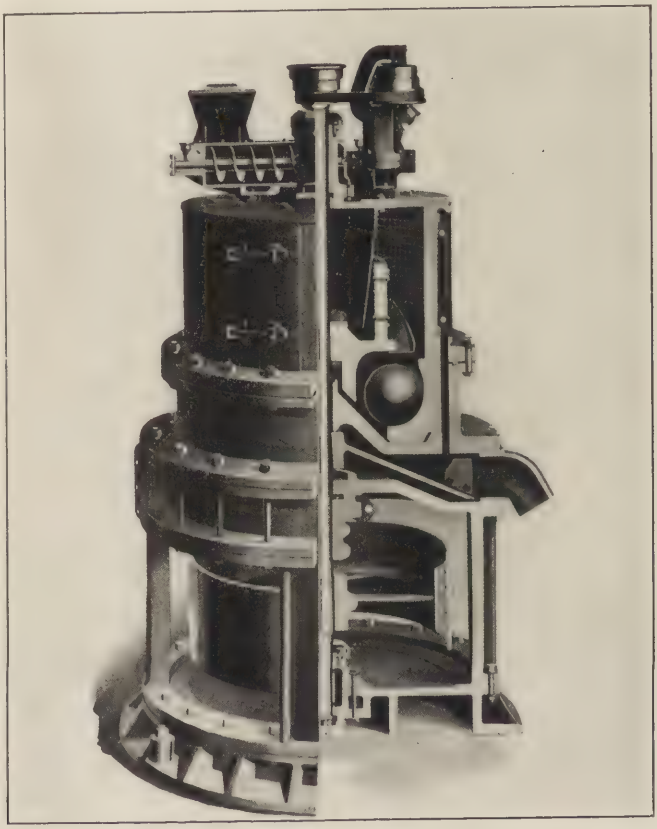


Fig. 66.—42″ Fuller mill, fan discharge type—pulley driven.

This machine is also made with an air separator mounted above the grinding unit. The type of mill first described, however, is the one which is most generally installed in the cement industry not only for pulverizing coal but also for grinding raw material and clinker. This mill is made in several sizes, the

smallest of which has a ring 24 inches in diameter and the largest of which has one 57 inches in diameter.

Table XXI gives the power required to operate and capacity when grinding dry bituminous coal of average hardness to a fineness of 95 per cent passing the 100-mesh screen.

TABLE XXI.—AVERAGE CAPACITY AND POWER REQUIREMENTS OF FULLER MILLS GRINDING BITUMINOUS COAL

Size mill Inches	Size feed Inches	Output in tons per hour	H. P. to operate
24	¾	0.5 to 0.6	10
33	¾	2 to 2.5	30 to 35
42	1	4 to 6	45 to 50
57	1¼	8 to 10	100
70	1¼	20 to 25	300

Where the Fuller mill is to be driven from a line shaft it is usual to employ an idler and quarter turned belt. When motor driven a vertical motor is generally used. The mills when used for coal are economical of power and repairs and can easily be adjusted to give a product 95 per cent of which will pass the 100-mesh screen. They take up a small floor space and cost less to install than most of the other mills.

In order to meet the demand for a mill of greater output than the types described above the Fuller-Lehigh mill has been redesigned so as to permit of the use of a 70 inch die. The large mill, however, retains the ball and die principle of grinding. Figure 67 shows the air type 70 inch mill with cover removed. It will be noted that the base plate which also forms the main housing of the mill, supporting all the grinding elements and the driving mechanism, is placed at the center of the mill in the same plane with the die and balls, thus forming the anvil block for backing up the die ring. This construction allows a lighter weight grinding ring than would otherwise be employed. The die ring is, of course, easily replacable.

The base plate of the screen type mill is provided with ports through which the finished material passes as is usual with mills of this type. In the air mill, however, no discharge ports are necessary and instead of fans on the mill shaft, the pulverized

material is removed by means of a separately driven exhauster. With either type of mill the gears for driving are housed under

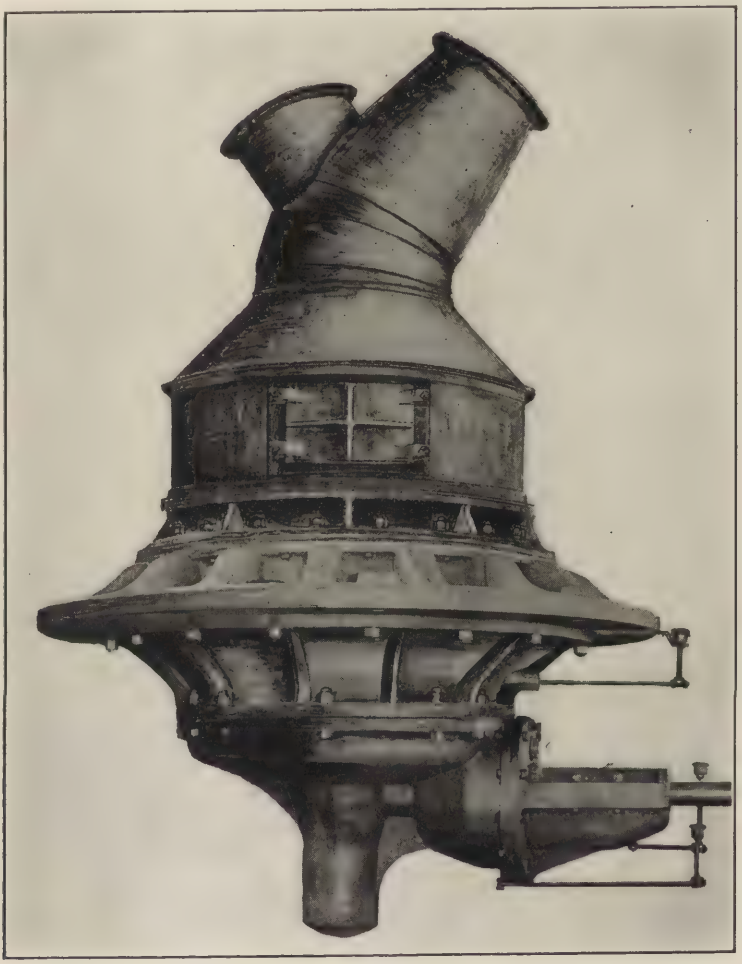


Fig. 67.—The 70″ Fuller-Lehigh mill, air type—Fuller-Lehigh Co.

the base plate and the shaft pinion may be directly connected to a motor through a flexible coupling.

The base plate rests directly on a reinforced concrete foundation, held down by six 3 inch anchor bolts. The actuating mechanism being below and the separating top section above the base plate a stable balance is produced in the mill structure. A large pit is provided below from which all of the driving mechanism is accessible. Provision has been made in both types of mills for the removal of the main shaft and all of the actuating mechanism through the top of the mill.

In the air separating mill, lifting fans are attached to the yoke above the balls and die for lifting the pulverized product into the separating chamber above the grinding element, so that the air current from the exhaust fan may separate the finished product from the unpulverized material as rapidly as reduced, passing it through the exhauster to a cyclone collector where the pulverized material collects while the air is returned through a central tube to the separating chamber, etc.

In the screen type pulverizer, lifting fan blades are provided above the grinding element for lifting the pulverized material to the vertical separating fan blades, which in turn pass the finished product from this separating zone through the protecting and finishing screens. The coarse material rejected by screens is returned to the grinding element, while the finished product passes through the screens to the annular space between the screens and the casing, and thence through the ports to the fan discharge chamber and out of the mill spout. Self-oiling bearings, and a screened circulating oiling system, are provided for the shaft in both types of mills, but the grinding element requires no lubrication. Means are provided for correctly adjusting the gear elements of the mill driving mechanism, and, in the case of the screen type mill, air inlets of the proper proportions are placed at the top of the mill for the circulation of the air needed for continuously passing the finished product through the discharge fan.

An independent feeding mechanism is attached to the supply bin which feeds the material to be ground through a flexible con-

nection to the mill, the rate of feed being based on the fineness required for the product.

The screen type mill has a capacity on cement raw material of 20 tons per hour when grinding to a fineness of from 80 to 85 per cent through a 200 mesh sieve, and on cement clinker a capacity of 50 to 60 barrels per hour at an equal fineness.

The mill is usually driven by a 250 to 300 horsepower motor direct connected to the shaft by means of a flexible coupling.

The 42-inch mill is the size chiefly employed in the cement industry for grinding raw materials and clinker. This size mill

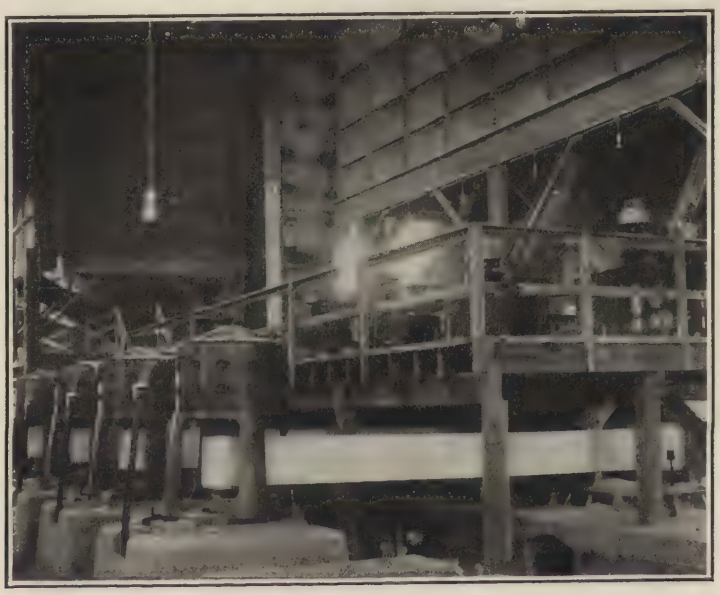


Fig. 68.—Fuller-Lehigh pulverizers with motors—Raw mill of the Tidewater Portland Cement Co., Union Bridge, Md.

has a capacity of from 4 to 6 tons of raw material and from 10 to 15 barrels of clinker. It requires from 60 horsepower in the former case to 75 horsepower in the latter. Figure 68 shows a battery of Fuller mills grinding raw material.

The Bonnot Mill

The Bonnot mill[1] is used for coal. It consists of a pulverizing unit, a separator, an exhauster fan and a collector. (Fig. 69). The grinding parts in this mill consist of a concave ring and four rolls. In the case of this mill, however, the ring is held vertically in the main frame, and the rolls revolve around inside of the ring

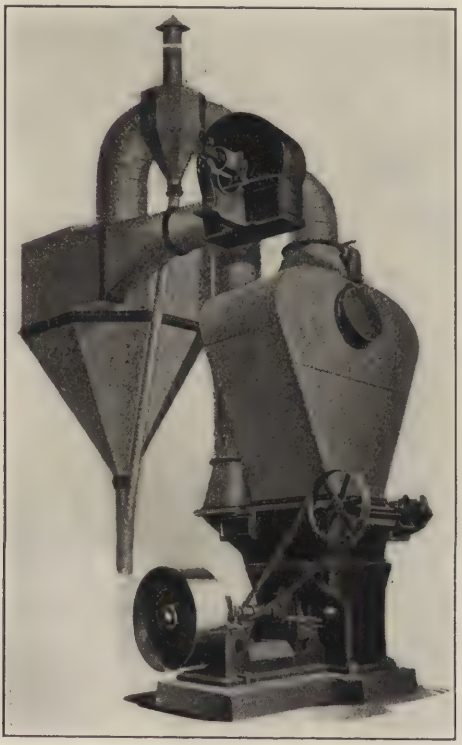


Fig. 69.—Bonnot coal pulverizer.

being held in position and driven by means of a driver. This latter is cast in one piece of hard steel and the rolls are not attached to this by bearings but merely rest in recesses or pockets in the driver.

[1] The Bonnot Company, Canton, Ohio.

This driver is also so shaped as to throw the material between the rolls and ring as it revolves. The air currents induced through the mill by the fan convey the material up into the separator. This latter consists of a cone-shaped receptacle made of galvanized steel plate which rests on top of the mill. In this the coarse material settles out of the air and drops back to the grinding unit while the fine material is carried out of the separator by the air and blown into the collector. The air after being freed from the coal particles is returned to the mill. The air separating and collecting part of the system are somewhat similar to that employed in the Raymond mill.

As is the case with the Raymond mill, it is possible to set this collector sufficiently high to dispense with the use of an elevator.

The manufacturers give the following as the output and horsepower requirements of the Bonnot mill when grinding bituminous coal of average hardness to a fineness of 95 per cent passing the 100-mesh sieve.

TABLE XXII.—AVERAGE CAPACITY AND POWER REQUIREMENTS OF BONNOT MILLS GRINDING BITUMINOUS COAL

Size Inches	Size feed Inches	Output in tons per hour	H. P. to operate
18	1	1¼	35
27	1¼	2½	60
36	1½	5	95

Kent, Maxecon and Ring-Roll Mills

These are mills which have so far been used in connection with some form of separator, both to prepare material for the tube mill and also to do the final grinding. The first two are manufactured by the same firm[1] and the Maxecon is an improved form of the older Kent mill. The principle of this type of mill is illustrated in Figs. 70 and 71 and consists of a vertical revolving ring, having three grinding rolls which are mounted on horizontal shafts and which press against the inner surface of the ring. The material to be ground is fed on the inner surface of the ring and is ground between this and the rolls. The inner surface

[1] Kent Mill Company, Brooklyn, N. Y.

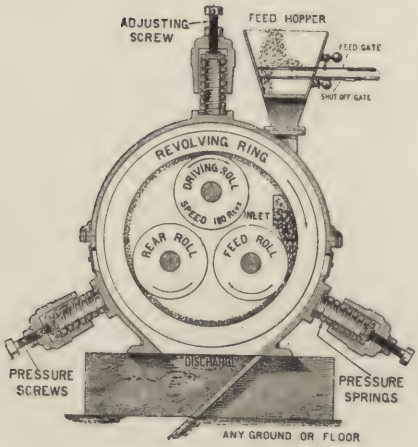


Fig. 70.—Kent mill.

Fig. 71.—Maxecon mills—Plant of the Altoona Portland Cement Co., Altoona, Kan.

of the ring is slightly concave and the cement is kept in the center of this and between the ring and rolls by centrifugal force.

The Mexacon mill requires 25 horsepower and has an output of 4 to 6 tons of limestone or 30 to 40 barrels of clinker ground to 20-mesh.

These two mills require the use of an outside separator; that is, the material as delivered by the mills themselves consists of both coarse and fine particles, and the latter must be separated from the mixture, and the former returned to the mills for further grinding. The manufacturers of the Maxecon mill have devised the "three-step Perfection Separator" for use with this mill. This is a vibrating inclined screen somewhat similar to the one described in the next section. At the plant of the Newaygo Portland Cement Co., where the Kent mill was used, the Newaygo screen, described on page 236, was devised for this purpose, but some plants employing the Kent mill used air separators, which

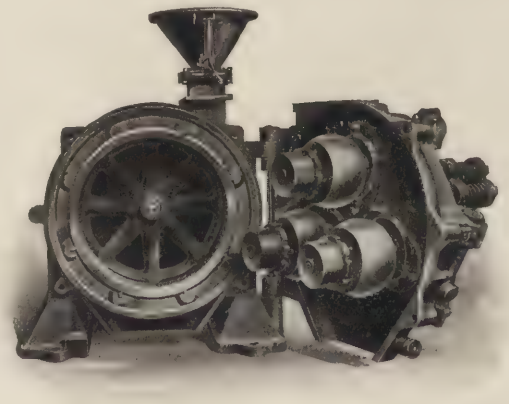


Fig. 72.—Sturtevant ring roll mill.

make use of a current of air to separate the fine from the coarse particles.

The Sturtevant ring-roll pulverizer[1] is somewhat similar to

[1] Sturtevant Mill Company, Harrison Square, Boston, Mass.

the Kent mill in principle, in that the grinding surfaces are in the vertical plane and consist of a ring and rolls. In the Sturtevant mill, however, the ring is fastened to a spider connected to a shaft and is driven by this and the front of the mill is hinged so that easy access to the interior may be had for repairs. (See Fig. 72).

Newaygo Separator

The Newaygo separator[1] consists of an inclined screen mounted at an angle of about 45°. The separating device con-

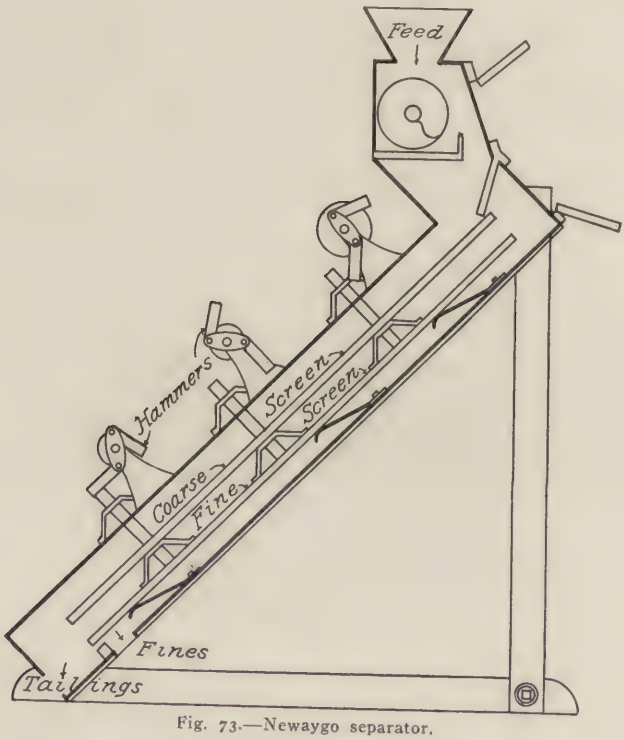


Fig. 73.—Newaygo separator.

sists of two sets of screens made of wire cloth, enclosed in a casing of steel plates. One of these screens is of coarse mesh

[1] Sturtevant Mill Company, Harrison Square, Boston, Mass.

and serves as a scalper to take off the large pieces and one screen is of fine mesh which acts as the final separator. The fineness is regulated by the mesh of this screen, although the product is always much finer than the screens. For instance a 60-mesh screen is used for a 100-mesh product. On this fine mesh screen, are mounted steel bands running from top to bottom. Similar bands are also mounted on the coarse screen. Short steel bars pass through the upper casing and also through the bands of the coarse screen and rest upon the bands on the fine screen. A shaft actuated by power runs across the top of the screen, outside the casing, and on this shaft are hinged short pieces of iron to form hammers. When the shaft turns, these hammers strike the short steel bars resting on the fine screen and the jar serves to bounce the fine material through and keep the screen from clogging. The material to be separated is fed on to the top of the screen by means of a screw conveyor which can be adjusted so as to feed this uniformly all along the width of the screen. The coarse material of course rolls over the two screens and is carried away by a screw conveyor at the bottom, while the fine drops through and slides down the casing in which the screens are enclosed and is carried away also by a screw conveyor. Fig. 73 illustrates the construction of the Newaygo separator.

Hummer Screen

The "Hum-Mer" Screen,[1] Fig. 74, is an inclined electrically operated woven wire separator in which the vibrations of the screen are produced by means of a high speed electromagnet instead of the hammers used in the Newaygo. This pulls the screen cloth upward with a sharp jerk and then releases the screen, the operation being repeated many times a minute. The wire screen itself is stretched very tightly on the frame and the combination of taut screen and electric vibration produces an intense, quick motion both toward and away from the magnet. The intensity of the vibration can be regulated. The magnet does not act directly on the woven wire cloth but instead on an iron band

[1] W. S. Tyler Company, Cleveland, Ohio.

fastened to this. The magnet is placed outside of the screen case in a dust-proof housing and may be tilted out of the way when it is desired to remove a screen. The magnet must be operated by direct current which will necessitate the use of a transformer at almost all cement mills. The "Hum-Mer" is built in units of 3 feet, each with its own electro-magnet. The

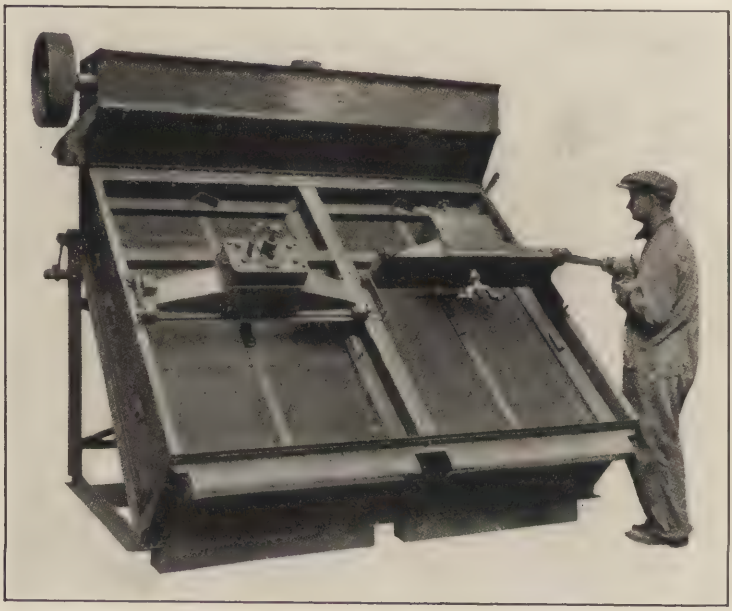


Fig. 74.—Hummer screen with electric vibrator, tilted—The W. S. Tyler Co.

screen is equipped with a screw to feed the material uniformly over its surface as is the case with the Newaygo. Usually two 3-foot units are bolted together to form a standard 6-foot "Hum-Mer" and provided with one common feeder. The vibrators require about one-half horsepower to operate each electro-magnet or 1 horsepower for each 6-foot "Hum-Mer." Slight additional power is required to operate the feed screw.

Air Separators

The Pfeiffer air separator is much used in Germany and Europe to take out the fine material from the product of the ball mill and so relieve the tube mill of some of its work. The separator is shown (in Section) in Fig. 75. It consists of an outer and an inner cone of sheet metal as shown in the drawing. The material to be separated is fed into the mill through the hopper on to a plate, which is connected to a vertical shaft, and is revolved at a speed of about 200 revolutions per minute. The material is thrown off this plate in a thin spray, by centrifugal force, and is met by a current of air, going in the direction shown by the arrows. The coarse particles fall through this current into the inner case, and the finer ones are carried into the outer space, between the inner and outer cones. The air currents are maintained by the fans as shown.

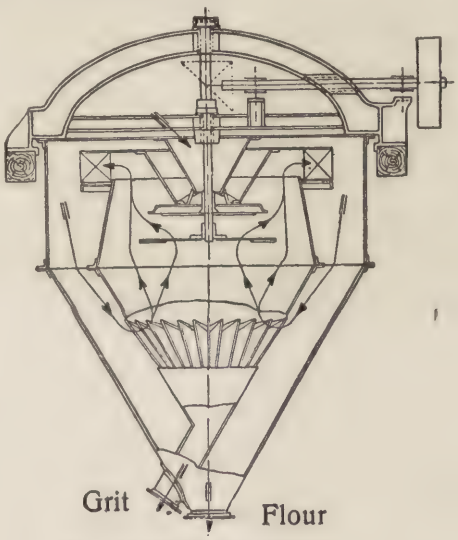


Fig. 75.—Pfeiffer air separator.

The Gayco-Emerick separator[1] is similar in principle to the Pfeiffer separator, but differs from it somewhat in details of construction.

[1] Rubert M. Gay Company, New York, N. Y.

Air separators, of both Pfeiffer and Emerick make were given quite an extensive trial in this country some years ago, both placed after the tube mill, and also after the ball mill. In the former case, the grit passed directly from the ball mills through the tube mills and from the latter to the separators. The fine material is sent from the separators to the stock house, and the coarse particles are returned to the tube mill.

At the time the first edition of this book was published, American cement manufacturers generally were giving the air separator a trial, in most cases installing the Emerick separator after the tube mill. At that time, some very good reports as to efficiency of the combination were given out both by the separator makers and certain cement manufacturers. In general, however, it may be said that air separators did not prove entirely satisfactory. While some few mills still use them, the majority of those who tried them have now given them up. They have been used to some extent in connection with the Kent mill, where as we have said, the need of an outside screen has made something of this sort necessary. Here they seem to have given as good satisfaction as the screen.

In Germany the Pfeiffers are installing separators at a number of works in connection with a short tube mill filled with steel balls. The product from the latter is fed to the separator which takes out the fine material and returns the coarse to the mill for further grinding. The separators are also used to reject the coarse material and give a very fine product.

As has been said the use of separators to take out the fine particles from the ball mill product and so relieve the tube mill of part of its work is quite general in Germany, but so far has not been tried to any extent in this country. A ball mill provided with 16-mesh screens of No. 3 wire will give a product containing between 15 and 20 per cent of material passing a No. 200 test screen. The Kominuter on the other hand gives a much larger percentage of fine material, as would be supposed since the material must travel from end to end of the drum before passing out, while in the ball mill it falls through the plates and

screens as soon as ground. A test of the Kominuter product made by the writer gave 25 per cent passing through a No. 200 sieve and 40 per cent through a No. 100 sieve. In this case the screens were 16-mesh and of No. 23 wire. A finer mesh screen on either ball mill or Kominuter will, of course, give a product containing more fine material. This fine material from the Kominuter contains considerable flour as sand briquettes made of the material passing a No. 200 sieve gave 335 pounds for seven days and 447 pounds for twenty-eight days. The material passing the No. 100 sieve gave 267 pounds for seven days and 320 pounds for twenty-eight days.

A rather amusing discussion of the separator question appeared in one of the engineering magazines, some years ago, the writer of which took the ground that the separators destroy the uniformity of the product and that, for example in a clay-limestone mixture, the lighter particles of clay would be blown away from the heavier limestone. The author seems to have overlooked the fact that by pulverizing the limestone particles a little finer they too will be blown out by fans of the separator so that while it may be true that on starting up a new separator the first product will be slightly overclayed, the trouble will be adjusted by the return of the limestone to the grinder for finer pulverizing, after which it will be blown out on its next passage through the separator *together with the clay from the new lot of mix fed into the tube mill*, the process being a continuous one. This same objection can be raised against ball mills, that the softer particles of clay or cement-rock will be pulverized sooner and drop through the screens of the ball mill before the limestone. In this case also this irregularity adjusts itself and in the same manner. My own personal experience with air separation at the plant of the Edison Portland Cement Co. convinced me that there is nothing against its use on the ground of lack of uniformity in the product. In both the Fuller-Lehigh and Griffin mills the separation of the finer from the coarser particles is effected by air separation, as fans are used in these mills to blow the fine material through the screen.

Capacity of Various Grinders

In the descriptions of the various grinding mills and crushers which have been given in the preceeding paragraphs, an effort has been made to show the approximate output of these various machines. These figures have been compiled from results obtained in actual practice and the output of the various machines is the average for long periods of time, but in all cases represents operating time only. An allowance should be made for shut downs occasioned by the need of making repairs, etc.

The condition of the material fed to the machine is an important item in determining the output of the crusher or grinding mill. Various raw materials differ among themselves very

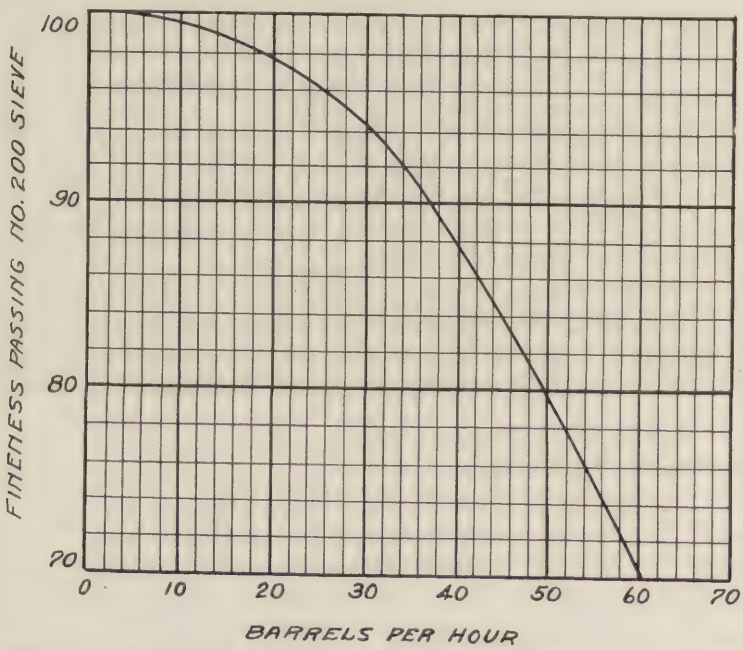


Fig. 76.—Relation between output and fineness of product, 5½ x 22 ft. tube mill.

greatly as to their hardness and some clinker will grind much easier than others. The amount of moisture in the material also effects very greatly the output of a grinding mill and with

crushers the amounts of clay and moisture effect their capacity. With crushers, too, it should be remembered that they are seldom fed continuously, and in most instances, they receive their material at irregular intervals, as when a car is dumped, etc.

The size of the material fed to the mill is also an important factor in determining the output of this—thus a tube mill fed with the product from a ball mill fitted with 14-mesh screens will not pulverize as much as it would if the ball mill had 16-mesh screens, etc. Limestone in the form of slabs will also crush more easily than will limestone in compact form.

The fineness of the product is an important item in determining the output of a mill. Fig. 76 illustrates graphically the relation between the output and the fineness of the product ground in a tube mill.

With the tube mill, another consideration is important, namely, the weight and nature of the grinding charge. The output will vary almost directly in proportion to the weight of this. Thus, referring to the Tables on page 209, a difference in the weights given in the last column will materially effect the quantity of the output and the horsepower necessary to operate and start the mills.

CHAPTER XI

BURNING-KILNS AND GENERAL DESCRIPTION OF THE PROCESS

Shaft Kiln

The first Portland cement made both in Europe and America was burned in upright or dome kilns, in which the raw material is moulded into bricks and charged alternately with layers of coke. The kiln is unloaded at the bottom and, after the clinker is drawn, it is carefully gone over by men or boys and the overburned and underburned sorted out and rejected. The properly burned clinker only is ground. These kilns are similar to those used for burning lime, and their form is shown in Fig. 77. From their shape they are also called "bottle" kilns. They

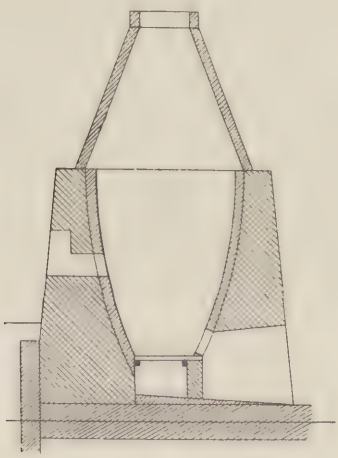


Fig. 77.—Dome kiln.

are intermittent in action, that is they must be freshly charged for each burning. On this account there is considerable loss due to the necessity of heating up the kiln for each burning. Saylor burned his first Portland cement in these kilns and the first mills in the Lehigh Valley all used this form of kiln.

In Europe where the bricks were made from the more or less plastic mixture of chalk and clay no difficulty was experienced in forming the bricks; in this country, however, the fine crystalline cement-rock did not have sufficient binding power of itself to make bricks of the strength to withstand the weight of the charge above them in the kilns, and it was found necessary to incorporate with it a small proportion of Portland cement, to give it binding power. At the American Cement Co.'s plant at Egypt,

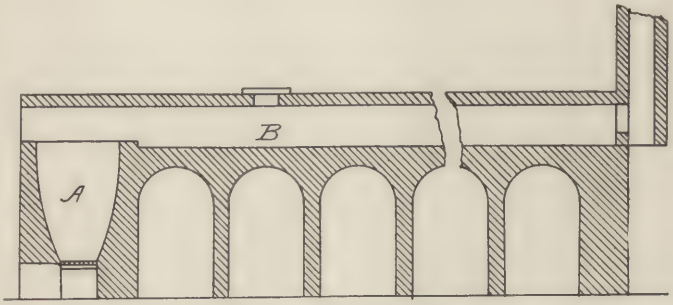


Fig. 78.—Johnston kiln.

Pa., the fine powder was mixed with liquid hydrocarbons to form a stiff paste, which was moulded by compression into bricks. This process saved drying the bricks and promised well, when the introduction of water gas raised the price of coal tar, and necessitated the abandonment of the scheme.[1].

The first efforts made to improve the "bottle" kiln were naturally to use the waste heat in the products of combustion coming off at the mouth of the kiln for drying the bricks. Fig. 78 shows the form of kiln invented in 1872, by Mr. I. C. Johnston, of Greenhithe, England, for this purpose. *A* is the kiln and *B* is the drying chamber. The kiln is charged with the bricks which have been dried by the heat of the previous burn. The wet bricks for the next charge are placed at the same time, in the tunnel-shaped

[1] For an excellent description of the process first used in the Lehigh District the reader is referred to an article "Looking Back to the Days of the Mud Floor," by Charles W. Erdell, in *Concrete*, Jan. and Feb., 1922, Cement Mill Section, also to "History of The Portland Cement Industry in the U. S.," by Lesley, Lober and Bartlett.

flue and the hot gases from the kiln pass over and around them, and dry them thoroughly. These kilns are, of course, more satisfactory than the ordinary "bottle" kiln, but they still waste much heat. The hot clinker, of course, carries off a great deal, and the cooling of the kiln itself causes additional waste. These kilns were installed in the original mill of the Western Portland Cement Co., Yankton, S. D.

The time lost in drawing the clinker, charging the kiln and heating it up, as well as the heat losses, led to the design of continuous kilns, in which the charging is carried on continuously at the top, and the clinker is drawn off from time to time at the bottom. Among the best known of these kilns are the Hoffmann ring kiln, the Schœfer and the Dietsch kilns, the latter two are modifications of the *etagen-ofen* or kiln of several stories. These kilns are economical of fuel, but require the material to be made into bricks for burning and the clinker to be sorted.

The Hoffmann kiln is shown in Fig. 79. It consists of a ring of chambers, built around a large central chimney. Each chamber is connected with the chimney by a flue and has a door opening outwards. The chambers are also all connected with each other. The bricks are piled up in the chambers, just as they are in a brick kiln, so that the products of combustion can pass around them and between them. The oven is operated as follows: When a chamber is loaded, it is shut off from the succeeding one, which is empty, by a sheet iron door, and connected with the preceding one. The flue leading into the chimney is also opened and the corresponding flue in the preceding chamber is closed. By this means, the waste heat from the compartment, whose contents is beng burnt, is passed forward, around the ring of compartments, to the one just charged, and thence through the flue and up the chimney. By this means the contents of the chambers are gradually heated up, the bricks are dried in the chambers near the flue and then become hotter and hotter as the chamber of combustion is brought nearer. The air for burning is passed through the chambers in which burning is completed and is thereby itself heated and the clinker cooled. It is usual to load one compartment each day, and of course, to

draw one. The fuel for burning is not loaded in with the bricks, but is fed in from openings at the top of the kiln during burning. The Hoffmann kiln is very economical of fuel, but requires much skilled labor if it is to operate successfully. The bricks have to be carefully piled and the charging requires skilled hands. This kiln was much in use in Germany, but so far as the writer

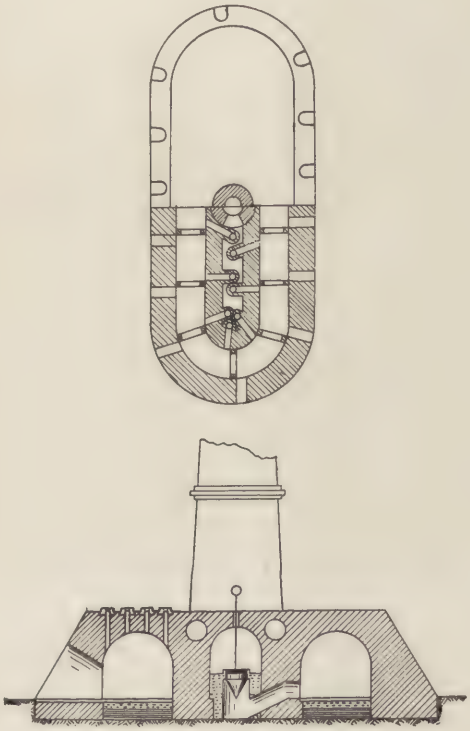


Fig. 79.—Hoffmann ring kiln.

knows, was never used in this country for burning Portland cement.

The Dietsch kiln is shown in Fig. 80. It was patented in 1884. It consists of a cooling chamber, *H*, a burning chamber, *F*, and a heating chamber, *C*. The kilns are usually built in pairs, back to

back. The kiln is loaded through the door, *A*, and as clinker is drawn out at the bottom, the dry slurry drops down into the heating chamber where it is gradually brought up to a high temperature. From the heating chamber it is raked over into the combustion chamber, by introducing a tool in the door, *E*, and fuel

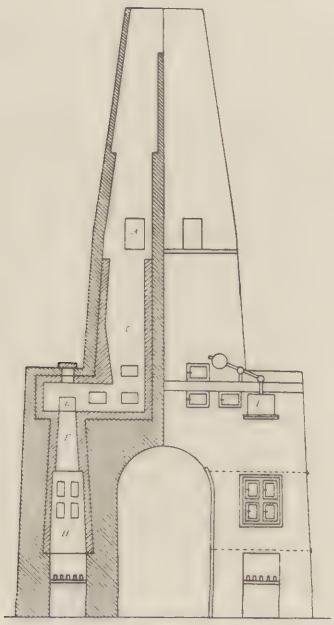


Fig. 80.—Dietsch kiln.

for the burning is mixed with it through the same door. The burning is completed in F. The cold air for combustion is heated by passing through the red hot clinker in *H*, cooling the latter. Eyes are placed at the lower levels of the combustion chamber, through which bars may be inserted to detach the sintered mass should it hang up, due to overburning. Several Dietsch kilns were introduced into this country in the early days of the industry, one being built for the Buckeye Cement Co., of Bellefontaine, O.

A modification of the Dietsch kiln perfected in Denmark and known as the Schoefer kiln, was introduced into several of the earlier cement mills and was once used, I believe, by the Glens Falls Portland Cement Co., Glens Falls, N. Y., exclusively, and

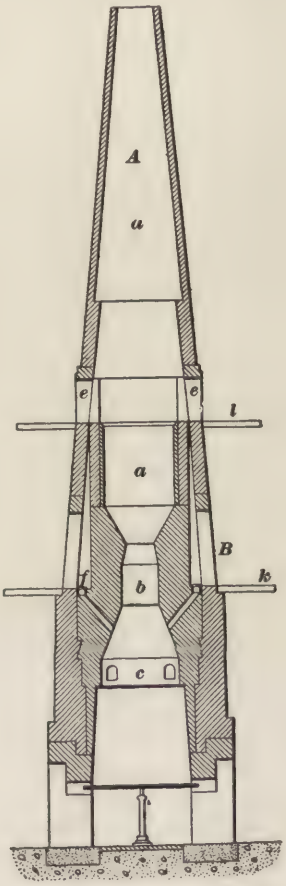


Fig. 81.—Schoefer kiln.

also by the Coplay Cement Co., at one of their mills, at Coplay, Pa., where eleven were once in use. The Schoefer kiln is shown in Fig. 81. It operates upon the same principle as the Dietsch kiln

and consists of a long vertical flue, the upper part of which serves as a preheating chamber, the middle narrow part as a combustion chamber and the lower section to heat the air.

With all these kilns the product has to be sorted and the underburned portions picked out and reburned. The clinker from them also often "dusts"—that is, falls to a powder on cooling. This fault is supposed to be caused by changes in the structure of the clinker brought about by too slow cooling of the latter. These shaft kilns require only about 45 pounds of coal per barrel, but the labor cost connected with them is two or three times as great as the fuel cost. The shaft kilns themselves cost in proportion to their output of clinker about twice as much as a rotary kiln.

The Rotary Kiln

The kilns above described are still used to some extent in Europe—particularly in the smaller and older works. In this country the cost of moulding the raw material into bricks was considerable, and the sorting of the clinker, made necessary by the uneven burning in these kilns, further increased the cost of manufacture. Abroad where labor is much cheaper than it is in this country, these operations could be carried on successfully, so that European cements could be brought to this country and sold in competition with American cements at a good profit. Their reputations were established and they could successfully hold their market against the home manufacturers, who could not afford to cut the price of their cement owing to the high cost of manufacturing due to the expensive labor item, so that all the early American manufacturers were seeking a cheaper method of burning, one that would do away with the employment of so much hand labor and allow them to compete successfully with their foreign rivals. This led them to experiment with the rotary kiln which had been invented in 1873 by F. Ransom, an English engineer, but which had never been successfully used in England. In this country the first plant to attempt its use was a small plant

in Oregon, in 1887, but the attempt proved a failure and the plant itself was shut down, owing to litigation among its stockholders.

About the same time the Atlas Portland Cement Co. began to experiment with Ransom's kiln, first at East Kingston, New York, on wet materials and later with success upon the cement-rock of the Lehigh District, at Northampton, Pa. At first, many difficulties were met with, and it was only after much experimenting, that they succeeded in making it work successfully. They found that owing to the shorter time during which the material underwent calcination, it was necessary to grind it much finer than had been necessary with the old bottle-shaped kilns. They also found it necessary to carry the lime a little higher, in their raw material than had been done before, and to moisten it slightly with water. In Ransom's original patent he proposed to heat the kiln by producer gas, but its development in this country was made possible, by the use of crude oil, as a successful method of burning powdered coal had not been perfected at that time. At first these kilns were only 40 feet long, but it was found more economical to lengthen them. Now from 125 to 250 feet is the usual length with 175 as the average at the newer plants.

General Description of the Rotary Kiln

The rotary kiln (Fig. 82) in its usual form consists of a cylinder from six to twelve feet in diameter and from 60 to 250 feet long, made of sheet steel and lined with fire brick. This cylinder is supported at a very slight inclination (a few tenths of an inch to the foot) from the horizontal, on two or more steel tires or riding rings which circle the shell and which in turn rest on heavy friction rollers. The cylinder is driven at a speed of from one turn a minute to a turn in two minutes by a girth-gear, situated usually near its upper end and a train of gears. The power may be supplied from a motor or a line shaft, but usually from the former. The upper end of the kiln projects into a brick flue which is surmounted by a brick lined stack.

Fig. 82.—Vulcan rotary kilns—Crescent Portland Cement Co.

The material to be burned is fed into the kiln in any regular manner through an inclined cast iron pipe, or by means of a water jacketed horizontal screw conveyor. The feeding device is usually attached to the driving shaft of the kiln, so that when the kiln stops rotating the feed also stops. The material entering the kiln works its way through this, due to the rotation of the cylinder and the inclination, the time required to pass through the apparatus depending on the speed of rotation and the inclination. The fully burned cement or *"clinker"* drops from the lower end of the kiln.

The lower end of the kiln is closed by a fire brick hood. This is mounted on rollers so it can be moved away from the kiln when the brick lining of the latter needs to be repaired. The hood is provided with two openings, one for the entrance and support of the fuel burning apparatus and the other for observing the operation, temperature, etc., of the kiln. The bottom of the hood is left partly open. Through this opening the clinker falls out and most of the air for combustion enters.

The kiln is heated by a jet of burning fuel introduced at the lower end, the material travelling in the opposite direction from the flame and the product of combustion. The lower end of the kiln is thus also a combustion chamber. Powdered coal is the fuel chifly employed but, in localities where they are as economical as coal, fuel oil and natural gas are used. The temperature of the hottest part of the kiln is about 2,600° F. It is rarely less than 2,400 ° F. or more than 2,800° F. The coal consumption varies from 80 pounds to 150 pounds per barrel of clinker, depending on the length of the kiln, the heating value of the fuel, whether the dry or wet process is employed and various other manufacturing conditions.

Having described the rotary kiln in a general way it may be well before going into the details of its construction and the various features of its operation to give in concise form the reactions[1] to be performed by this piece of equipment.

[1] In connection with the chemistry of cement burning the reader is referred to Chapter II on "The Chemical Composition of Cement," p. 24, *et seq.*

Reactions which Occur in the Kiln

The reactions which occur in the burning of cement clinker have been quite carefully studied by Rankin[1] at the United States Geophysical Laboratory. On entering the kiln the mixture is first dried, next the carbonates are decomposed and the sulphur and organic matter burned away. When the hot mixture of lime, silica and alumina enters the clinkering zone, there are first produced those silicates and aluminates of lime which form most readily, in other words at lowest temperatures. These compounds are $5CaO.3Al_2O_3$ and $2CaO.SiO_2$. These are probably formed in the order given, since the aluminate melts at a lower temperature than the silicate. Neglecting unessential elements we then have in the mix.

$5CaO.3Al_2O_3$
$2CaO.SiO_2$
CaO

The first two compounds next unite in part with the third, lime, to form the tricalcium silicate and the tricalcium aluminate.

At the temperature obtained in the ordinary cement kiln, the compound $5CaO.3Al_2O_3$ will completely change to the compound $3CaO.Al_2O_3$. The compound $2CaO.SiO_2$, however, is not completely converted to the compound $3CaO.SiO_2$, partly because there is not sufficient lime present to form the latter compound.

Our present knowledge of the composition of Portland cement is not sufficient to let us say with certainty as to what proportion of the final clinker should be dicalcium silicate and tricalcium silicate respectively. In most commercial cements, however, the two silicates are present in about equal quantities. We, however, do know that free lime should not be present to any extent and that the reaction in the kiln should be carried to the point where practically all of the free calcium oxide has united with dicalcium silicate to form the tricalcium silicate. Whether it would be of advantage to carry a higher percentage of tricalcium silicate is a point which must be proved. Originally it was supposed that the larger the amount of tricalcium silicate

[1] *Jour. Ind. and Eng. Chem.*, Vol. VII, page 446, *et seq.*

present in cement the higher the quality of the latter. Recent investigations, however, attribute to the dicalcium silicate certain desirable qualities.

To sum up there are two important series of chemical reactions to be effected in the kiln:

1. The decomposition of the carbonates of lime and magnesia into the oxides of these two metals.
2. The recombination of these oxides with silica and alumina to form the three essential compounds of Portland cement —tricalcium silicate, tricalcium aluminate and dicalcium silicate.

To carry out the first series of reactions, namely the breaking up of the carbonates, it is necessary for heat to be supplied to the raw material at the rate of approximately 950 B. t. u. per pound of clinker formed.[1]

To carry out the second reaction, the forming of the silicates, however, it is only necessary to heat the materials entering the burning zone up to a temperature of approximately 2,500° and to maintain them at this temperature or at a slightly higher temperature until the three compounds are formed. During this time the materials themselves give off 200 B. t. u. per pound of clinker.[2]

The Four Zones

The kiln may be roughly divided into four zones according to the work done in each:

In the first zone the mix is being heated to the temperature at which the carbonates decompose. In a wet process plant, the water is being evaporated also in this zone. Various secondary reactions occur here, such as the burning of the sulphur and the organic matter in the mix, both of which give off heat, and the liberation of the combined water and moisture in the raw materials, which reactions take place at comparatively low temperatures.

[1] See page 290.

[2] See page 291.

In the second zone the carbonates are decomposed. This occurs in that part of the kiln which is at a temperature of approximately 1,650° F.

In the third zone the material has been freed from its carbon dioxide and is being heated to the temperature necessary for the formation of the aluminates and silicates of lime.

In the fourth zone the cement clinker is formed—that is, the silicates and aluminates of lime. This zone is also the combustion chamber for the fuel.

It must not be supposed that these zones in the kiln are separated by any well defined lines. They unquestionably overlap and some of each reaction takes place in the adjacent zones.

Generally speaking, in a dry process kiln we may consider 25 per cent of the length of the kiln as used to heat the material up to the point at which the carbon dioxide is driven off; 50 per cent of the kiln is utilized largely to drive off carbon dioxide, while 25 per cent constitutes the clinkering zone. In a wet process kiln the first zone is a somewhat greater percentage of the length and succeeding zones somewhat smaller percentages of this.

Mechanical Details of Construction[1]

The kiln shell is made of open-hearth steel plates. These vary in thickness with the size of the kiln but range generally from one-half to three-fourths inch thick. With small kilns the sections of the shell are one sheet to the round but with large kilns 8 feet and over are two sheets to the round. This forms the strongest and most rigid construction obtainable and is superior to a shell made in sections of three or four long sheets to the section with only a few circumferential joints. All joints are butt type, edge of plate to edge, all edges squared, and are made with butt-straps which are usually of a trifle heavier plate than the shell itself. These entirely encircle the kiln. Each butt-strap adds strength The longitudinal joints are not in continuous line but are staggered, that is on adjacent sections they are on opposite sides.

[1] Much of this information was furnished by the late Mr. J. T. Jeter, Engineer of the Vulcan Iron Works, Wilkes-Barre, Pa.

The riveting must be well done and the rivets fit the holes tightly and be securely driven. The thickness of the plate composing the shell and the thickness and width of the butt-straps must be proportional to the length and diameter of the shell together with the weight of the brick lining and the material being burned. In a short kiln (under 80 feet), the thickness of the plate is usually the same throughout the shell, but in long kilns, the thickness of the plate in those portions of the shell at either end which overhang the tires may diminish as it approaches the feed and discharge ends. The greatest bending strain comes directly under and midway between each tire. It is well to use in large kilns wider butt-straps here and two or three rows of rivets on each side of the joint. Other joints including longitudinal joints have generally two rows of rivets on each side of the joint.

The shell usually has one or more angle iron rings riveted on the inside, one of which is near the discharge end to take up the thrust of the fire brick lining. Where Sil-o-cel is used between the brick and the shell it is also well to rivet an angle lengthwise through the entire length of the kiln. The discharge end of the kiln is usually provided with a cast iron brick retaining ring. This is made in segments and bolted on so the brick can be slipped in place endwise. A cast iron ring known as the *"feed-head"* is also fastened to the feed end.

Most kiln manufacturers have their own ideas as to where the riding rings should be placed, but the following formula[1] will give the approximate position for almost any make of well designed kiln.

First tire (from feed end)	0.24 × Length
Second tire (from feed end)	0.84 × Length
or	
Upper Overhang	0.24 × Length
Middle Section	0.60 × Length
Lower Overhang	0.16 × Length

Each tire is supported upon a set of four rollers, mounted in pairs on two cradles or rocker arms. These latter automat-

[1] Vulcan Iron Works, Wilkes-Barre, Pa.

ically adjust themselves in such a way that an equal amount of pressure is always imposed upon each rollor. The rollers are removable and can be easily replaced if broken. Fig. 83 shows the method of supporting. The cradles are provided with an adjustment and by cutting them so that one pair of rollers is at

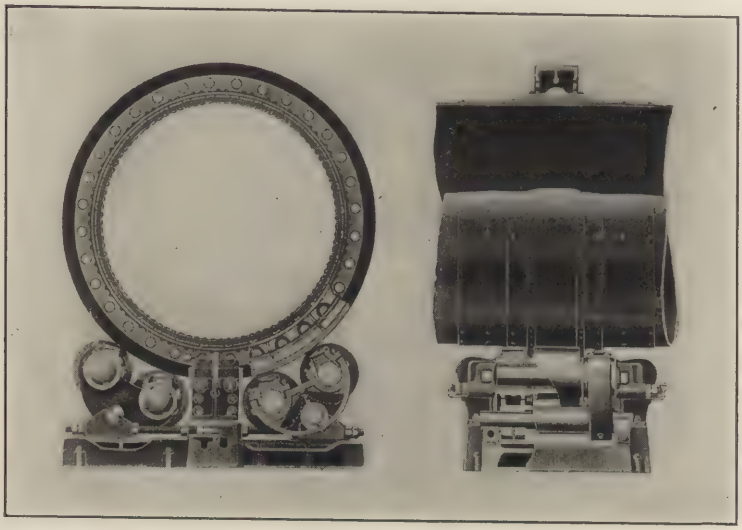


Fig. 83.—Method of supporting kiln—tire and bearings. Vulcan Iron Works.

a slight angle to the tire the kiln may be made to run up or down on the rollers as desired. By proper adjustment the shell can be made to run true.

In order to take up the lateral thrust of the kiln and keep it on its bearings, at least one set of thrust rollers is used. This consists of two horizontal rollers which bear one on each side of the tire. The roller shafts revolve in bearings located on the same base with the rocker arm and supporting rollers. The thrust rollers are placed at the tire nearest the girt-gear.

The girt-gear or gear-ring is usually cast in two or more sections in order to permit of replacements. In the case of large cement kilns, a cross-section of the gear is usually in "T" shape.

The gear is bolted to a flange ring also of the "T" section but inverted which in turn is riveted to the shell. The latter is provided with a reinforcing band at this point.

The drive gear consists usually of a train of gears having a reduction ratio of from 100 to 1 to 220 to 1, that is for one revolution of the kiln the driving shaft makes from 100 to 220 depending on the size of the kiln. The final reduction is through a pair of bevel gears, which places the drive shaft at right angles to the kiln. This shaft may be driven from a motor either by direct connection through a speed reducer and flexible couplings or by a belt or silent chain drive.

The firing hood is made of angle iron and steel plate and is to be lined with fire brick. The hood is usually mounted on four wheels. These usually rest on rails set in the floor. This permits the hood to be rolled entirely away from the end of the kiln when it is desired to repair the lining of the latter, etc.

Stack and Dust Chamber

The upper end of the kiln extends into the "Dust Chamber." (See Fig. 84). The latter may be made of brick properly stayed with channel iron buckstays and tie rods, or it may be made of reinforced concrete. If of the latter it should be lined with fire brick and it is well to use a layer of Sil-o-cel blocks or other heat insulator between the fire brick and the concrete. The dust chamber is usually provided with one or more doors through which the dust which collects in the chamber may be removed. These also act as dampers when they are opened. A screw conveyor is usually run in front of the cleanout doors and the dust is conveyed to the feed boxes or slurry tanks by means of this and an elevator.

Where waste heat boilers are used, a seal ring[1] is employed to prevent air from leaking in where the kiln projects into the dust chamber.

Each kiln is usually provided with its own stack and this rests on the dust chamber. Occasionally one stack is used for a bat-

[1] See Chapter XV, for description of such a seal.

tery of kilns but this is not usual. Even where waste heat boilers are used, a stack is generally provided so that the kiln may be operated without the boiler should occasion arise. The stack

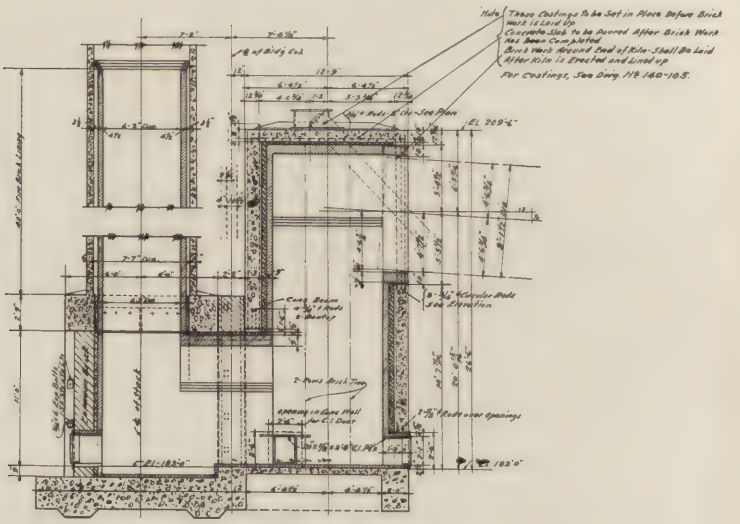


Fig. 84.—Reinforced concrete stack chamber. Designed by author.

is always lined with brick. Steel stacks are generally used but if properly designed and built concrete stacks are better as they do not have to be painted. The diameter of a stack for any kiln may be found from the formula.[1]

$$E = \frac{B \times K}{16.65\sqrt{H}}$$

$$d = 13.54\sqrt{E} + 4$$

When E = effective area in square feet, H = height of chimney in feet, B = barrels of cement burned per hour, K = 90 for dry process kilns and 130 for wet process kilns, and d = interior diameter in inches. In steel stacks, an allowance should be made for the fire brick lining, or in other words the stack should be $d + 8$ inches.

[1] Derived from Kent's formula.

For example, an 8 x 125 foot dry process kiln will produce about 30 barrels per hour. If the stack is made 70 feet high, then

$$E = \frac{30 \times 90}{16.65 \sqrt{70}} = \frac{2700}{139} = 19.5$$

$$d = 13.54 \sqrt{19.5} + 4 = 63.8$$

Allowing 8 inches for brick lining, the stack should be 72 inches.

Length and Diameter

The first rotary cement kilns to be generally employed were 6 feet diameter by 60 to 80 feet long. Thomas A Edison was the first person in this country to attempt a kiln longer than 80 feet, those at his plant at Stewartsville being 150 feet long. These kilns were put in operation in the fall of 1903 and proved entirely practical and effected the economy in fuel which Edison had promised they would. His experiment was watched with great interest, and, as soon as the success of these longer kilns was known, several of the mills then under construction lengthened their kilns to 80 feet. This plan has since been tried by most of the older mills who extended their kilns to 100 or more feet. All of the mills built since this time have installed kilns longer than 100 feet, some of them being 250 feet long.

Kilns are usually made of the same diameter throughout their length, although some of them have the clinkering zone bigger than the rest of the kiln. That is to say the feed end is made of smaller diameter than the discharge end. Sometimes kilns taper through 10 to 20 feet at the feed end to a diameter somewhat less than the rest of the kiln.

The relation between length and diameter, on the one hand and capacity and coal consumption on the other, is pretty well understood and we have had an increase in the size of kilns during the last two decades with a view chiefly towards obtaining greater outputs per kiln. The greater the diameter of the kiln, the more coal we can burn in it and consequently the greater the output. The theory of the long kiln is that the greater the length of the kiln the more opportunity will be given to the ma-

terials to absorb the heat from the products of combustion, and to a lesser degree, greater time will also be given to effect the combination of the oxides with the silica and alumina to form the calcium aluminates and silicates.

The smaller the diameter of the kiln the more intimately are the gases brought in contact with the material both directly and through the medium of the hot walls of the kiln. If a kiln 60 feet in diameter is increased to 100 feet an immediate economy will be effected. If at the same time, however, the diameter of the kiln is also increased very little, if any, saving in fuel will be effected. In fact, if the diameter is increased too much an actual increase in the quantity of fuel required to burn a barrel of cement will be required.

Unfortunately there is a structural objection in making kilns of small diameter and great length and generally in order to obtain a kiln which is mechanically satisfactory it is necessary to increase the diameter to some extent as the length is increased.

In comparing the performance of two kilns, it is well to consider the ratio between the area of the cross-section of the kiln, lining to lining, that is, in a kiln 8 feet in diameter by 125 feet long with a 6-inch lining the ratio between the length and the area as 125 is to 38.5 or 3.2 : 1. This gives us a better method of comparing kilns than that ordinarily used. The size kilns most popular are as follows:

TABLE XXVII.—Sizes of Rotary Kilns Commonly Employed in Cement Burning.

Diam.	Length	Area of cross-section of burning zone, 6" brick lining	Ratio length to area, 6" brick lining
6	60	19.64	3.1 : 1
7	100	28.27	3.5 : 1
8	125	38.49	3.2 : 1
9	150	50.27	3.0 : 1
9	175	50.27	3.5 : 1
9	200	50.27	4.0 : 1
10	175	63.62	2.8 : 1
10	200	63.62	3.1 : 1
10	250	63.62	4.0 : 1
11	250	78.54	3.2 : 1

By referring to this table it will be seen that considerable difference exists between the length: area ratio in kilns commonly employed. The writer has observed that the fuel consumption of kilns, other things being equal, is in inverse order to this ratio. From this we would expect a kiln 7 x 100 feet to be considerably more economical of fuel than one 6 x 60 feet and this has been found to be the case. On the other hand, a kiln 9 x 150 feet will be no more economical of fuel than one 6 x 60 feet and experience shows this also to be true.

Longer kilns are usually employed in wet process plants than in dry process plants. The reason for this is that in the former process the upper end of the kiln acts as a dryer. By making the kilns longer the drying can be effected more economically; the increased length allowing the heat in the gases to be utilized more completely in evaporating the water, due to the longer period of contact between the gases and the slurry.

Since the chief reason for length in the kiln is to utilize more completely the heat in the gases it is probable that present practice has seen the limit for kilns of the diameters now in use. This is due to the fact that the gases can now be successfully employed for steam generation, and the waste heat boiler offers a more efficient method of utilizing the waste heat in the gases than does the lengthening of the kiln. Present practice would seem to indicate for the dry process a kiln with a length: area ratio of about 3: 1, followed by a waste heat boiler. For the wet process a kiln with a slightly higher ratio might be used.

Where power can be purchased cheaply or generated hydro-electrically and fuel is high, long kilns will no doubt be employed to advantage.

The length of a two support kiln can not be conveniently made greater than sixteen to eighteen times the diameter. A kiln with two supports is now advocated by most authorities as preferable to one with three or more. It is obviously less difficult to get and keep two supports in line than it is to get three or more. Considerable distortion of the kiln can (and does) occur without effecting the carrying mechanism when two supports are em-

ployed. If there are more than two, however, any warping will result in a transfer of the load from all three supports to only two and indeed momentarily while this transfer is being made to only one. This condition tends to spring the shell and break the supports. Where greater length is desired, the shell can be made in two sections, connected together by a link and driven by the same motor, etc., the upper section usually revolving the lower. Each section is supported by two tires. Several such kilns are now in use.

Feeding the Raw Material Into the Kiln

Dry material is fed into the kiln by means of an inclined spout or a water-jacketed screw conveyor running from large bins,

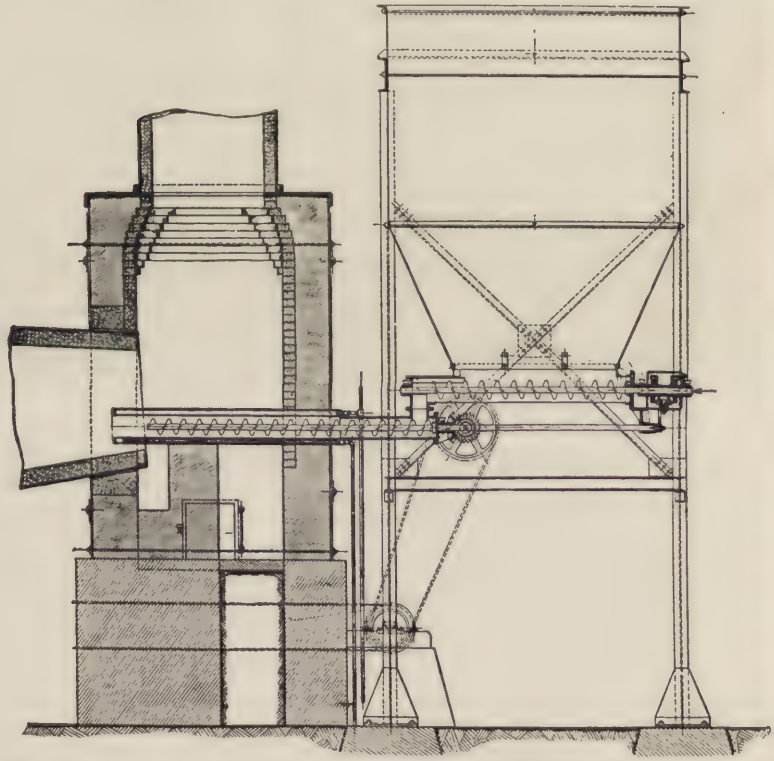


Fig. 85.—Stock bins and water-jacketed conveyor for feeding raw material into kiln.

which are situated usually over or just back of the flue, through the latter, far enough into the kiln to prevent the materials falling into the flue when the kiln revolves. The feeding device is usually attached to the driving gear of the kiln, so that when the latter stops the feed is shut off.

Fig. 85 shows an arrangement designed by the Allis-Chalmers Co. for feeding the material into the kiln by means of a water-

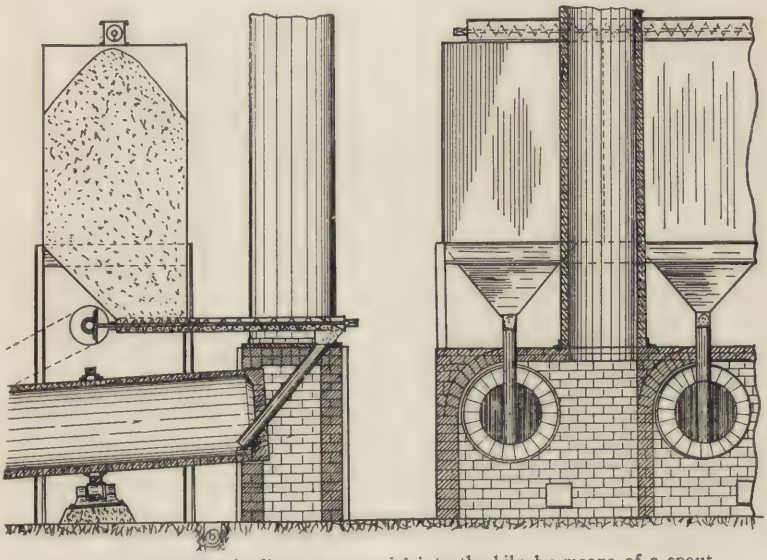


Fig. 86.—Method of feeding raw material into the kiln by means of a spout.

jacketed conveyor. This plan is now considered inferior to the method of spouting the material into the kiln. Fig. 86 shows the arrangement generally employed where the latter plan for introducing the material into the kiln is followed. It will be noticed that the bins are located above the kilns. This saves room. The long conveyor leading from the bins to the hopper spout insures a regular feed of material to the kiln. The stack is set to one side of the center line of the kiln which gives the dust a chance to settle. Another arrangement of the stack is shown in Fig. 84. The spout is of cast iron pipe.

Slurry is usually fed in by means of what is known as a "Ferris Wheel" feeder. Referring to Fig. 87 it will be seen that this consists of a series of buckets, *a*, similar to those used on an elevator, fastened to a wheel, *b*, the wheel being rotated by a pair of gears, *c*, which in turn are driven from the kiln shaft or

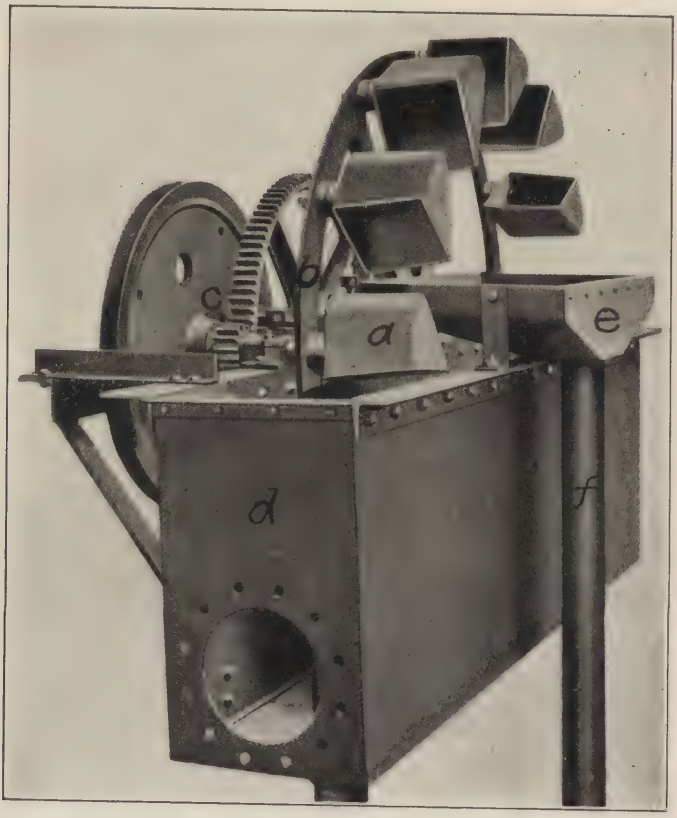


Fig. 87.—"Ferris wheel" for feeding slurry to kiln—Allis-Chalmers Mfg. Co.

by a variable speed motor. The slurry is kept at a constant level in the tank, *d*, by means of a pump and an overflow pipe returning to the kiln feed basin. Occasionally the slurry is kept in a kiln feed basin located above the feeder and is run from the

former into the latter by gravity. In this case, the level of slurry in the tank, *d*, is maintained by means of a float valve. The buckets, *a*, dipping in the tank, *d*, as the wheel revolves, fill with slurry and elevating this to the point where they are turned over, discharge the slurry into the hopper, *e*, which leads to the kiln through the pipe, *f*. The amount of slurry fed may be varied by altering the speed of rotation of the wheel, by removing some of the buckets or even by altering the angle at which these are placed on the wheel making them pick up less slurry as they leave the tank.

Another form of feeder employed occasionally consists of a needle valve operated by a wire cable so that it can be operated from the front end of the kiln. Still another type of feeder consists of a spiral pipe somewhat similar to the sampler for cement described in the section of this book on cement testing.[1] In the writer's opinion these feeders are not so satisfactory as the "Ferris Wheel" described previously.

In both the wet and the dry process, what is required of the feeder is that it shall deliver the material to the kiln in a regular amount. The slurry feeders all do this very nicely. With the screw feeders, however, used for dry material, the rate of feed is often irregular and sometimes the kiln is flooded with a rush of material and at others the material arches in the bins over the screw feeder and the bin sides must be rapped to break these arches. Flooding usually occurs when the bins are nearly empty, while "arching" may be avoided by making the hopper bottoms of the bins with at least one straight side and better with three straight sides. The screw feeder should be as long as a convenient location of the bins will allow.

Kiln Lining

The rotary kiln as has been said is lined with fire brick. This brick should be of the most refractory kind. I believe at one time a magnesia brick was used but now a good quality fire brick is considered as satisfactory and more economical than the ex-

[1] See Chapter XVII.

pensive magnesia lining. A good fire clay brick should analyze within these limits:

	Per cent
Silica, SiO_2	45.0 to 50.0
Alumina, Al_2O_3	43.0 to 48.0
Iron, Fe_2O_3	Less than 3.0
Magnesia, MgO	Less than 0.5
Lime, CaO	Less than 0.5

It should also be free from iron and alkalies, since these cause fusibility. A fire brick lining should last, if carefully attended to, at least 9 to 12 months and sometimes they go even longer than this. At the end of this time the bricks are eaten away nearly to the iron shell and it becomes necessary to cut away the brick from the first 20 or 30 feet of the kiln and reline this portion. The upper part of the kiln lining, or that portion of it which merely comes in contact with the powdered raw material before sintering commences, usually lasts indefinitely. In kilns working on wet materials it is sometimes the practice to leave the upper 20 or 25 feet of the kiln unlined since this part of the kiln is kept fairly cool by the wet slurry. Sometimes channel irons or Z bars are fastened to the sides of the kiln to form shelves for drying the material.

A bauxite or alumina brick, manufactured by the Laclede-Christy Clay Products Co., St. Louis, Mo., has been extensively used in the west and middle west for lining Portland cement kilns and it is, in that section at least, considered superior to the silica brick.

In place of fire brick, a concrete or clinker brick made from Portland cement clinker and Portland cement is sometimes used. The clinker should be screened and that portion of it passing a one-fourth inch screen used. This is mixed with Portland cement in the proportions of thirty parts clinker to twelve parts cement and made into a medium wet concrete. This is then rammed into wooden forms of the proper size and shape and allowed to harden. The bricks are ready for use several days after making. One large mill in the Lehigh District used these bricks exclusively at one time for lining the clinkering zone of their kilns, and found them

very satisfactory. Under conditions in this region, however, they do not seem to be any cheaper than fire brick. They also do not stand up well where the kiln is not run continuously.

The fire bricks used to line the lower end of the kiln are usually from 6 to 9 inches thick, and those for lining the upper end, from 4 to 6 inches. These bricks are keyed to fit the circle of the kiln.

In the old upright kilns, it was the usual practice to coat the lining of the kiln with a "grout" of slurry, so that it was natural for something of the same sort to be tried with the rotary kiln. It was soon found that a certain amount of the raw material could be made to adhere to the fire brick lining of the kiln, thereby protecting the bricks from the scorifying action of the caustic clinker. It is now the practice to burn entirely on coated bricks. When this coating falls off, usually only in patches, the kiln is heated up above the normal temperature, raw material is scraped down over the bare spot and pounded into place with a heavy iron bar. Water is then usually run on the "patch" to harden it. In some mills salt is used on the bare spot, as it is supposed to make the patch hold better. The writer has never seen any advantage in its use, however.

The fire brick are held in the kiln by a heavy angle iron running around both ends of the kiln. This also helps to stiffen the kiln shell.

The ordinary kiln brick is 9 inches long at the end nearest the shell, and 4 inches wide or three circles of brick per linear foot of kiln. The number of brick required to line a kiln, etc., may be found from Table XXIII. No allowance has been made in this table for breakage and other loss.

Mr. W. S. Landis, formerly of the metallurgical department of Lehigh University but now of the American Cyanamid Co., first called general attention to the large loss of heat due to radiation from the kiln shell and suggested placing a coating of some efficient non-conductor of heat between the shell and the fire brick. The writer many years ago tried placing asbestos board between the shell and brick. He found then that while

radiation losses were reduced, the life of the lining was decreased, partly because the asbestos board flaked under the pressure of the brick and allowed the latter to loosen up, but more particularly because the asbestos confined the heat to the lining and caused the latter to burn out in the clinkering zone more quickly than it would if it was allowed to dissipate its heat by radiation.

The radiation losses from a cement kiln shell is shown in Fig. 92,[1] page 304. In this diagram the vertical lines show the temperature of the shell and the horizontal lines the loss of heat in the British thermal units (B. t. u.) per hour per square foot of kiln surface. In making use of this data, the kiln is usually divided into ten or more sections and the temperature of each is taken and the surface of each calculated. The heat lost in each section is then the product of its surface area and the heat lost at the determined temperature per square foot as shown in Darling's table. The heat lost by radiation from the entire kiln is, of course, the sum of the heat lost by all the sections. When kilns are exposed to the weather as is now sometimes the practice, the loss shown by Darling's curve should be multiplied by 1.3 for wind and by 1.7 for rain and wind.

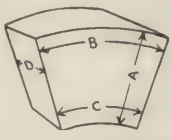
It is now considered good practice to place a layer of 3-inch Sil-o-cel blocks between the fire brick and the shell throughout the kiln with the exception of the twenty-five feet nearest the discharge end. If the Sil-o-cel is used here the lining is destroyed rapidly. Cooling of this portion of the lining by radiation appears to be necessary if the ordinary kiln brick are to last. The Sil-o-cel are laid flat and great care must be used to get both the Sil-o-cel and the fire brick in tight. The Sil-o-cel lining probably reduces the radiation losses to from 25 to 50 per cent of what they would be without such heat insulation. It also increases the temperature of the waste gases from 200° to 300° F. above what they are without it. This is important where waste heat boilers are employed as it materially increases the amount of steam which can be obtained from the waste gases. The quantity of Sil-o-cel blocks required to line a kiln may be calculated from Table XXIII.

[1] C. R. Darling, *Engineering* (London), March 14, 1919, p. 643.

The lining must be carefully put in with tight joints. The best method is to lay a ring at a time, without mortar in the joints, wedging each ring securely. After the bricks are in place they are slushed over with a thin grout of cement and water.

Continuous kiln operation, with constant load and temperature conditions, and material to be burned of uniform composition, tend to lengthen the life of the lining. Shut downs, variable feed, material first high in lime and then low, cause a loss of coating and consequently damage to the brick; as each time the coating falls it carries away with it some of the surface of the fire brick.

TABLE XXIII.—Dimensions and Number of Standard Rotary Kiln Blocks Required to Line Rotary Kilns of Various Diameters



Dimensions of standard blocks	Dimensions of and number of blocks for kiln and diameter shown below						
	6′ 0″	6′ 6″	7′ 0″	7′ 6″	8′ 0″	9′ 0″	10′ 0″
Standard 6″ Block							
A—Dimension in inches	6	6	6	6	6	6	6
B—Dimension in inches	9	9	9	9	9	9	9
C—Dimension in inches	7.500	7.625	7.719	7.813	7.875	8.000	8.125
D—Dimension in inches	4	4	4	4	4	4	4
Diam. outside circle, ins.	72	78	84	90	96	108	120
Diam. inside circle, ins.	60	66	72	78	84	96	108
Standard 9″ Block							
A—Dimension in inches	9	9	9	9	9	9	9
B—Dimension in inches	9	9	9	9	9	9	9
C—Dimension in inches	6.750	6.938	7.063	7.188	7.313	7.500	7.656
D—Dimension in inches	4	4	4	4	4	4	4
Diam. outside circle, ins.	72	78	84	90	96	108	120
Diam. inside circle, ins.	54	60	66	72	78	90	102
Numger of block to circle	25	27	29	31	33	38	42
Number of block to line One linear foot of kiln	75	81	87	93	99	114	126
Number of block to line One linear foot of kiln where 3″ Sil-o-cel block is used between kiln shell and fire brick	69	75	81	87	93	108	120
Number of 4½ x 9 x 3 in. Sil-o-cel blocks required for insulation per linear foot of kiln when laid flat	67	73	78	84	90	102	114

Speed of Rotation

The kilns are rotated in different mills at different speeds, varying from one turn in one-half a minute to one turn in three. The average, however, is from a turn in a minute to one in two minutes. The speed varies somewhat with the angle at which the kiln is pitched, the greater the pitch the slower the speed, as the steeper the angle of the kiln the greater distance the material will travel with each revolution.

Usually the speed can be regulated by some arrangement of an automatic speeder, such as the Reeves, the Mosser speeder or, where run from separate motors, by a controller. In some mills all the kilns are on one shaft and consequently of fixed speed. There are some points in favor of each. Where the speed can be regulated by the burner, he has better control of the burning, but there is sometimes a tendency on his part, where the foreman is lax, to cut down the speed and consequently the capacity of the kiln in order to make his own work easier. Where there is a likelihood of the mix not being regular, speeders should always be put in, as it is easier to control the burning of such material by the kiln speed than by the coal feed. With line shaft, the kilns are arranged with some sort of jaw clutch, so they can be cut out for patching, relining, etc. It is also necessary occasionally to shut them down for "heat" if the mixture burns hard, or the raw material is fed into the kiln irregularly, causing it to become overloaded. As we have said, the raw material fed into the kiln should be controlled by the speed of the latter and be shut off when the kiln stops.

Most of the newer mills are installing individual motor drives for their kilns, employing for this purpose slow variable speed motors. The power requirements to operate kilns of various sizes is about as follows:

6 x 60 ft.,	1 to 3 R. P. M.,	5 to 7 H. P.
7 x 80 ft.,	1 to 2 R. P. M.,	8 to 12 H. P.
8 x 125 ft.,	¾ to 1½ R. P. M.,	15 to 20 H. P.
9 x 150 ft.,	⅜ to ¾ R. P. M.,	22 to 30 H. P.
10 x 170 ft.,	¼ to ½ R. P. M.,	30 to 40 H. P.

A great deal has been said about the proper speed for a kiln to revolve, no two authorities agreeing, and the writer has come to the conclusion from personal experience that this will depend largely upon the material, how it burns, etc. If the kiln is run at a high speed, the material travels through in a thin stream and remains in the kiln but a short time. On the other hand, it is being continually turned over and exposed to the hot kiln gases and kiln lining, so that while the time of heating is shorter the chances of absorbing heat are greater.

Inclination of the Kiln

The inclination of the kiln affects, of course, the rapidity with which the material travels through the former, other things being equal. The speed with which the material travels is also affected by the rate at which the kiln is rotated. If two kilns were inclined, one say at an inclination of three-fourth of an inch to the foot and the other one-half of an inch to the foot, the material could be made to travel through both at practically the same rate of speed by revolving the latter much faster than the former. On the other hand in the case of the more level pitch the kiln would carry a much larger body of material and consequently the material would remain in the kiln for a longer time. This point is worth considering where trouble is experienced with the soundness of the cement, as by increasing the time in the kiln a more effective combination of the lime with the dicalcium silicate can be effected.

The inclination of the kiln in practice usually gets less as the kiln increases in diameter. Kilns 6 and 7 feet in diameter are usually pitched at about three-fourth inch to the foot, 8-foot kilns at five-eighth inch to the foot and 9-foot kilns and larger at one-half inch to the foot.

Length of the Clinkering Zone

The length of the clinkering zone is usually from 15 to 20 feet. A ring usually forms at the upper (feed end) of this and below this ring the formation of the clinker takes place. The

fire brick here are usually coated with from 3 to 5 inches of sintered material as this is the portion of the lining most subject to destruction. It is in this section of the kiln that the tricalcium silicate and aluminate are formed.

The clinkering zone is also the combustion chamber. Here the fuel is burned, and the length of the clinkering zone is determined by the length of the flame.

Theoretically the length of the clinkering zone is effected by the fineness of the coal or the efficiency with which oil is atomized, the thoroughness with which the air for combustion is mixed with the fuel, percentage of volatile matter in the coal, etc. Practically the length of the zone is a matter of draft. This is usually regulated by the doors at the base of the stack chamber; or if waste heat boilers are employed, the fan on the latter. If the doors at the base of the stack are opened, this acts as a damper and crowds the clinkering zone nearer to the front of the kiln. Slowing down the draft fan if this is employed has a similar effect.

Capacity of Cement Kilns

Most tables showing the capacities of cement kilns have been compiled from results obtained in practice with little or no attempt to reconcile the various figures so given. Manifestly the only way to determine the relative output of kilns is to compare them when working under *exactly* similar conditions. It is, of course, difficult to compare more than a few sizes of kilns in any one plant, and so it is necessary to collect data from many plants in order to cover the wide range in size of cement kilns. It is evident that burning conditions vary widely in different plants and hence this data to be satisfactory must be reconciled to some standard condition. The most convenient form in which to place the result of this study of kiln capacity so it can be used for reference is in the form of an algebraic formula, the solution of which will express the average approximate capacity of a cement kiln of a given size. In using any formula, it should be borne in mind that local conditions influence greatly the capacity

and that any figures obtained are general and may not apply closely to any given case.

Various attempts have been made at different times to devise a formula for determining the capacity of the rotary cement kiln.

Engineers of the Portland Cement Association use the following formula

$$C = \frac{PL}{4}.$$

When P = the circumference taken inside the lining, L = length in feet and C = capacity in barrels per twenty-four hours.

Eckel in his work[1] gives the following formula for dry process kilns.

$$C = D^2 \times \frac{L}{8}, \textit{maximum}$$

$$C = D^2 \times \frac{L}{12}, \textit{minimum}$$

When C = capacity in barrels per day, D = diameter in feet and L = length in feet. With this formula there is quite a divergence between the two extremes and the upper limit is far higher in the case of large kilns than any capacities actually met with in practice.

The writer has kept careful notes on the performance of kilns in all parts of the country and after careful study of this data devised a formula which he and his associates have used for many years in their work. The figures obtained by it check quite closely with average practice except in the case of very large kilns, 11 and 12 feet in diameter. It is doubtful, however, if these large kilns have been pushed to their limit in cases which have come under the writer's observation. The formula is purely empirical and is as follows:

$$C = (\tfrac{3}{4}\, L + 15) \times A \times 0.17.$$

When C = Capacity in barrels per day of twenty-four hours, L = length of kiln in feet and A = area cross-section excluding lining or $\left(\frac{\text{Diameter} - 1}{2}\right) \times 3.1416$.

[1] Limes, Cement and Plaster, by Edwin C. Eckel.

Table XXIV showing the capacity of rotary kilns has been calculated from this formula.

All of the above formulas refer to dry process kilns. Wet process kilns have from 60 to 75 per cent of the capacity of dry process kilns.

TABLE XXIV.—Capacities of Rotary Cement Kilns

Dry Process

Diam.	Length—feet						
	60	80	100	110	125	150	200
6′–0″	200	250	300	325	360	—	—
6′–6″	240	300	360	390	440	525	—
7′–0″	280	360	430	470	525	600	—
7′–6″	—	420	500	550	600	725	925
8′–0″	—	490	575	625	700	825	1,075
8′–6″	—	550	675	725	825	950	1,225
9′–0″	—	—	775	825	925	1,100	1,400
10′–0″	—	—	975	1,050	1,175	1,375	1,775

Wet Process

Diam.	Length—feet						
	60	80	100	125	150	200	250
6′–0″	140	175	210	250	—	—	—
6′–6″	170	210	250	310	370	—	—
7′–0″	200	250	300	370	420	—	—
7′–6″	—	295	350	420	510	—	—
8′–0″	—	—	400	490	580	755	—
8′–6″	—	—	—	580	665	855	—
9′–0″	—	—	—	—	770	980	1,220
10′–0″	—	—	—	—	960	1,245	1,540

The capacity of a cement kiln is influenced by many factors among which are (1) the skill of the operator, (2) the fuel and method of burning, (3) the draft, (4) the chemical composition of the material, (5) the moisture in this, particularly in the case of slurry, (6) the fineness of the material, and (7) the degree of burning, etc.

Fuel Requirements

The fuel requirements of the rotary kiln vary among other things with (1) the moisture in the materials burned, (2) the chemical composition and fineness of the raw material, (3) the length and diameter of the kiln, (4) the skill of the operator, (5) the heating value of the fuel and its nature, (6) radiation losses

from shell, etc. In general it may be said that the fuel required will increase with the moisture in the slurry—dry materials requiring much less fuel than slurry. The fuel requirements also decrease with the length of the kiln provided the diameter remains the same. Conversely if the diameter increases and the length remains constant the more fuel is needed. Some materials require more fuel than others, due to chemical characteristics. Material high in lime is harder to burn than material low in lime. The fuel requirements are in inverse proportion to the heating value of the fuel; 40 per cent more coal with a heating value of 10,000 B. t. u. per pound would be required than of one with a thermal value of 14,000 B. t. u., etc. Table XXV gives the fuel consumption of various kilns. The figures are average results over a period of time. They include the coal used for heating the kiln after patching and the usual shut downs and delays met with in every mill. The figures in the tables are for coal containing 14,000 B. t. u. per pound and oil with 140,000 B. t. u. per gallon.

TABLE XXV.—Fuel Consumption in Cement Burning

Kiln dimensions	Dry process		Wet process, 35% water	
	Coal per barrel, lbs.	Oil per barrel, gals.	Coal per barrel, lbs.	Oil per barrel, gals.
6 x 60	110	11.0	140	14.0
6 x 100	88	8.8	118	11.8
7 x 100	94	9.4	124	12.4
8 x 125	97	9.7	127	12.7
9 x 150	100	10.0	130	13.0
9 x 175	94	9.4	124	12.4
9 x 200	88	8.8	118	11.8
10 x 175	102	10.2	132	13.2
10 x 200	99	9.9	129	12.9
10 x 250	88	8.8	118	11.8
11 x 250	100	10.0	130	13.0

Labor

The operation of Portland cement burning is essentially a skilled process and a skilled workman is required to attend it. He must know just how the clinker should be burned and have a good eye for "heat," so that he can tell when his kilns are hot enough

to clinker the raw material properly. The placing of the patches and the coating of a freshly lined kiln also require some skill. To be economically run the kilns should be kept at as nearly a uniform temperature as the irregularity of the feeding devise will permit. Kilns run spasmodically, first hot, then cold, require much coal, turn out poorly burned clinker, and require much patching. Since patching requires the stopping of the kiln the output is also cut down.

The burner should also be a sufficiently good mechanic to look after the mechanical part of his kilns. One burner usually looks after two to four kilns. The operations of the interior of the kiln are watched through darkened glasses. No efforts have been made to use pyrometers since the temperature must change with the refractoriness of the material, etc., and the heat is entirely judged by the incandescence of the interior of the kiln and the clinker as observed through these glasses.

The method of injecting the fuel into the kiln and the preparation of the powdered coal are described in the next chapter.

Degree of Burning

Properly burned Portland cement clinker is greenish black in color, of a vitreous luster and usually when just cooled sparkles with little bright glistening specks. It forms in lumps from the size of a walnut down, with here and there a larger lump. Underburned clinker, whether this is due to a low temperature in the kilns or an overlimed mixture lacks the vitreous luster and the glistening specks. The *failure* to sparkle, however, is not necessarily characteristic of underburned clinker, though the sparkle itself is never seen in underburned clinker, as the rate of cooling etc., effects this somewhat. If much underburned, the clinker is brown, or has soft brown or yellow centers. Low limed clinker unless very carefully burned, usually has brown centers also, but is hard and glassy. The two should not be mistaken; the clinker with *soft* brown centers is underburned that with *hard* brown centers is underlimed.

Overburned clinker shows the same characteristic as underlimed,—the hard brown centers. I have never seen that the quality of cement was injured any by overburning, unless the material was low in lime when the resulting cement was apt to be "quick-setting," but the proper degree of sintering is far enough to carry the process and to burn any harder is not only a waste of coal for burning, but also for grinding since the hard brown slag like clinker is very hard to pulverize.

Properly burned clinker should have a specific gravity of at least 3.15 and when rapidly pulverized and ignited show a loss of under 1 per cent; although neither of these tests is of any value in determining the thoroughness of burning, when applied to ground cement.

CHAPTER XII

BURNING—SCIENTIFIC CONSIDERATION OF THE PROCESS

Chemical Changes Undergone in Burning

The chemical changes undergone during burning may be summed up as follows:

All of the water originally present whether free, hydroscopic or combined is driven off and the carbon and organic matter in the raw material are also burned away.

The carbon dioxide, existing in the raw material in combination with the lime and magnesia as carbonate of these elements, is practically entirely expelled. Even the little which exists in freshly ground, well burned cement is probably most of it absorbed from the air, since cement very rapidly absorbs carbon dioxide and water.

The iron, the greater part of which is usually present in clay and cement-rock in the ferrous condition is almost completely oxidized.

The sulphur whether present in the raw material as sulphide, sulphate or in combination with organic matter is much of it expelled and the remainder is usually all of it, except a mere trace, found present as calcium sulphate. This is to be expected since calcium sulphate gives off its sulphuric acid, when heated with silica. Indeed, I believe it has been proposed to make cement by heating together a mixture of clay and gypsum, the sulphuric anhydride driven off during the process being caught and condensed with water and sold for sulphuric acid. It has also been supposed that the sulphur of the coal entered the clinker. This is erroneous, since the amount of gas slack necessary to burn 100 pounds of clinker will contain sufficient sulphur to make the clinker analyze at least 1.5 per cent SO_3 if it were all absorbed, while as a matter of fact clinker seldom analyzes anywhere near this amount.

The alkalies, potash and soda are partly expelled in the kiln. In experiments made by the writer, which will be detailed later,

the losses of soda amounted to from 19 to 28 per cent, while those of potash ran from 46 to 52 per cent.[1]

This loss of alkali is also shown by analysis of the deposit collecting on the walls of the kiln stack, a sample of which contained:

	Per cent
Soda	1.38
Potash	6.83

Influence of Coal Ash on Chemical Composition of Cement

In a paper read by the author before the Association of Portland Cement Manufacturers, the results of an experiment to determine the losses actually occurring in the rotary kiln were given. This experiment consisted in sampling carefully the raw material going into the kiln, the clinker coming out and the coal used for burning. Three separate tests were made and the results compared. As the result of this experiment, it was found that the silica, ferric oxide and alumina are increased by approximately one-half the coal ash. Undoubtedly, in the rotary kiln much of the ash is carried out with the gases by the strong draft of the kiln. This we would expect when we consider that the particles of ash are of the same volume as the particles of coal, and yet only one-tenth their weight, for when the coal burns it leaves its ash in the form of a skeleton. These particles of ash are already in motion and are in the full draft. The gases have a velocity of at least 2,000 feet per minute, which is quite enough to carry the particles up the chimney. It seems probable in view of these facts that what ash does contaminate the clinker, comes from the impinging of the flame upon the material in the kiln. The ash strikes the clinker and its velocity is stopped by the impact and it either falls among the clinkers or it sticks to the red-hot, semi-pasty mass. It is probable that the coarser the coal the more ash will contaminate the clinker. It is an important point where this ash falls. If it falls before the raw material begins to ball up, 24 pounds extra limestone should be added to every 600 pounds of raw material to take care of the ash, as in this case,

[1] See page 317.

it would form Portland cement clinker. If, however, it falls on the clinker after it forms into balls, this quantity should be very much less, if any at all, as its action would then most likely be merely on the surface of the clinker to form a slag and not a true Portland cement clinker.

The above changes are simply those which we can detect by comparative chemical analysis of the raw material and the clinker. None of them is sufficient of itself to form Portland cement. All the carbon dioxide can be driven off the raw material and still Portland cement clinker will not be the result. For this it is necessary that the lime combine with the silica and the alumina, and in order for this combination to take place it is necessary for the material to be heated to a considerably higher temperature than that necessary to drive off carbon dioxide. If a small sample of raw material is heated to a constant weight over an ordinary laboratory blast lamp, very little, if any, clinkering will take place, except, perhaps, on the under side of the sample next to the crucible, yet all the carbon dioxide will have been driven off. The various opinions as to the constitution of Portland cement clinker have been fully detailed in Chapter II on the chemical composition of Portland cement, and it is unnecessary here to repeat them.

Wm. B. Newberry made an experiment[1] of great interest as tending to throw some light on the question of what takes place during the passage of the raw material through the kiln.

During a temporary shutdown of one of the rotaries at the Dexter Portland Cement Co., at Nazareth, Pa., the kiln was allowed to cool down without being emptied and samples of the charge were then taken from every four feet throughout the length of the kiln.

After careful examination these samples were analyzed, the results showing the changes which take place in the composition at successive stages of the burning. The raw material used was cement-rock without the addition of any other material. The first sample was of unburned raw material taken at the point of entering the kiln and the last (No. 14) was the finished clinker

[1] *Cement and Engineering News*, Vol. XII, No. 5.
See also Soper, *Amer. Soc. Mech. Engrs.*, 1910.

within four feet of the discharge at the lower end. Fig. 88 shows graphically the chemical charges which occurred in this experiment.

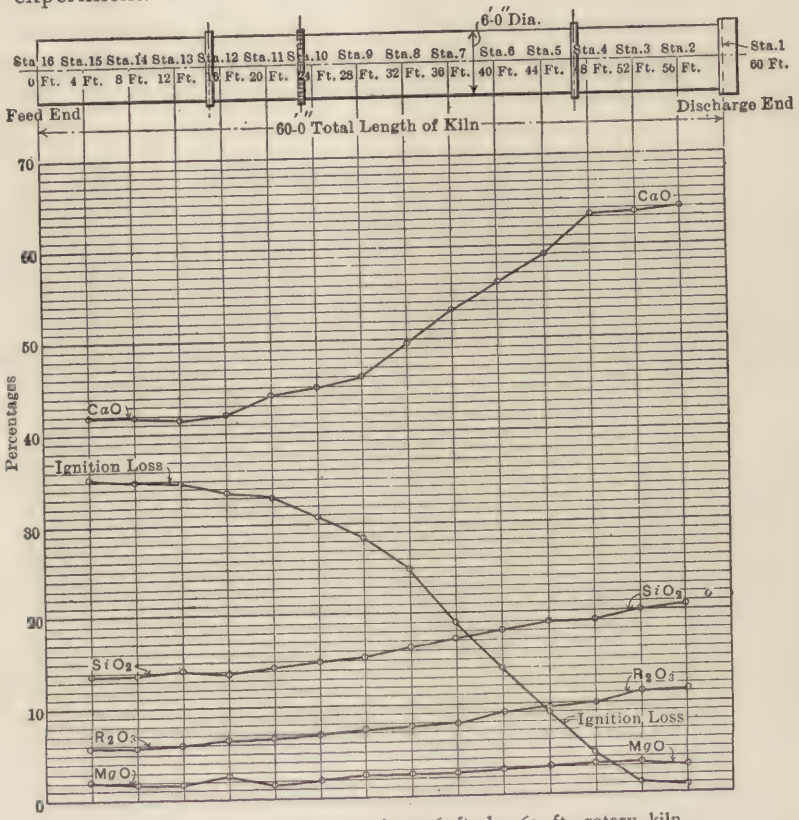


Fig. 88.—Chemical changes in a 6 ft. by 60 ft. rotary kiln.

The physical change from raw stone to clinker is shown by the characteristics of the different samples given below:

"Nos. 1, 2 and 3, blue gray powder, changing to buff between 3 and 4.

"Nos. 4, 5 and 6, yellowish buff powder, commencing in 6 to ball up into small lumps.

"Nos. 7, 8, 9 and 10, yellow to brown balls like marbles; soft, easily crushed in the fingers, becoming darker and harder toward 10.

"No. 11, lumps quite hard and brown, traces of sintering on surface, softer inside.

"No. 12, lumps brown and partly sintered, beginning to lose regular rounded forms hard.

"No. 13, larger lumps, irregular and rough, almost black. Very noticeable difference between 12 and 13, latter is like brownish clinker and is burnt throughout.

"No. 14, smaller and more rounded lumps, black, has all the appearance of finished clinker, in fact, no further change is seen as it leaves the rotary."

Relation Between Time, Temperature and Fineness

In the formation of clinker, the materials are never actually melted and the combination is brought about by the intimate contact between surfaces. This is affected by three things, the amount of surface exposed, or in other words, the fineness of the raw materials, temperature to which the material is heated and the time during which it is maintained at this temperature. These three conditions are intimately associated as has been pointed out previously. With very finely ground material the combination will take place at a lower temperature or with less heating than where materials are coarsely ground. With materials of the same fineness the combination will take place more rapidly where the temperature is higher, conversely the time required to bring about the combination will be the longest where the temperature is lowest or the grinding insufficient.

Attention has been called previously to the expression of this law in the form of a mathematical equation.

$$D \times T \times F = C$$

In which D represents time, T temperature, F fineness and C a consonant, namely, clinker. If we increase any one of the three variables D, T and F it will decrease one or both of the other two, thus by increasing the time in the kiln we decrease the temperature necessary to clinker or the fineness, while if we grind the materials more finely we decrease either the temperature or the length of time in the kiln and may thus increase the output of the kiln or decrease the fuel required per barrel. This equation does not take care of the chemical composition of the mix and is intended to express rather the physical than the chemical relations

in burning. It also must be understood that the materials must be heated to the temperature at which clinker will form. It has been both practically and theoretically demonstrated that this condition does exist in cement burning.

There is a very practical point in connection with the temperature of the kiln which must be considered, and that is the ability of the lining to stand the temperature. As a matter of fact, the lining not only has to stand the temperature, but also the chemical action which occurs between the lime and the aluminates from which fire brick is made. This affinity is marked at high temperatures.

This brings up the point of the possibility of using another lining for the kiln rather than the ordinary high alumina clay brick. In the early days of the industry, the rotary kilns were lined with magnesia brick. This lining was succeeded by the present lining of high alumina clay brick. The question naturally presents itself as to whether any better results would be obtained by the use of other brick, such for example as carborundum brick. Great improvements have been made in the manufacture of fire brick of a very high degree of refractoriness. It is possible that cement manufacturers may be overlooking something and that better results might be obtained than is now possible by the use of some of these materials. This is a point which, however, can only be determined by experimenting.

Temperature of Burning

The temperature of the clinkering zone of the cement kiln as determined by optical pyrometers is generally found to be between 2,525° F. and 2,650° F. with about 2,600° F. as an average. In looking over quite a wide range of temperature measurements made by the author and covering both wet and dry process kilns, various raw materials, and kilns of sizes ranging from 6 x 60 feet to 9 x 200 feet the actual temperatures of the clinkering zone when the kiln was operating normally and turning out a well burned product were found to range from 2,545 to 2,640 with 2,585 as the average. The size of the kiln made no

difference in the temperature nor did the process employed or the raw materials.

Soper[1] measured the temperature at various points in a kiln 7 x 100 feet by means of a Le Chatelier pyrometer by inserting

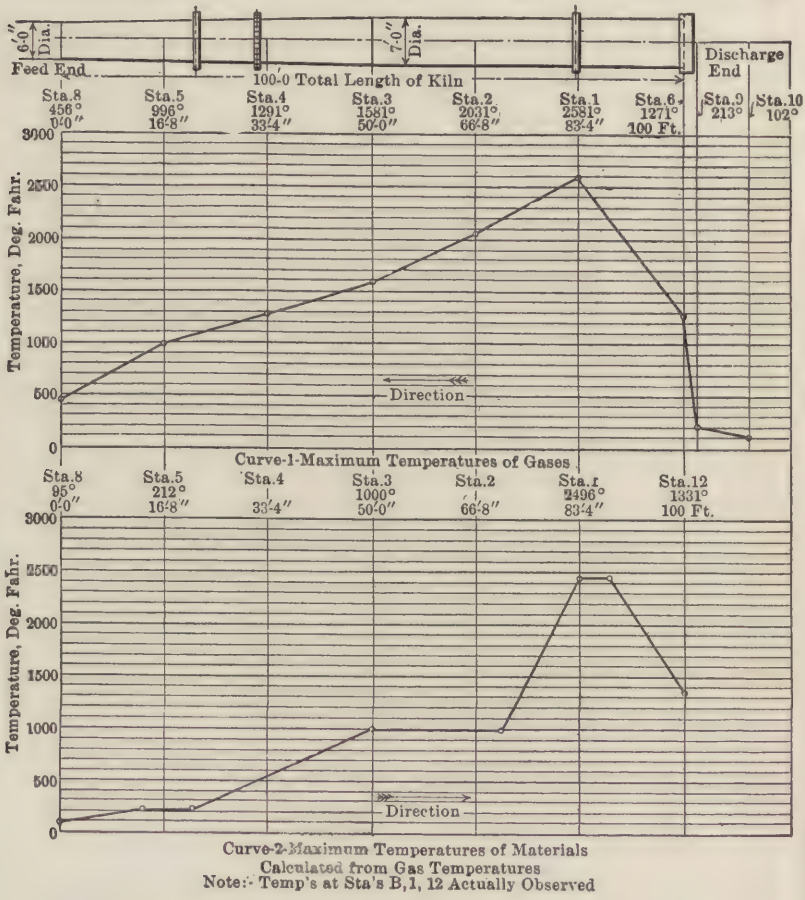


Fig. 89.—Temperature of gases and Materials in a 7 ft. by 100 ft. rotary kiln, wet process.

the porcelain tubes containing the elements through holes previously drilled through the kiln shell and fire brick lining. This

[1] Paper read before Western Society of Engineers, Nov. 15, 1905.

kiln was working upon wet materials. Fig. 89 shows the temperature of the gases at various points in the kiln as ascertained in this test.

Campbell[1] made some interesting experiments on the relation between the chemical composition, temperature, time and fineness of the raw material on the burning of cement. He found that the lower the lime: silica ratio the more easily the material could be burned, that the time in the kiln affected the temperature necessary and that the finer the material was ground the lower the temperature necessary for properly burning. Campbell's experiments were made in a small laboratory kiln[2] and the temperatures he employed were somewhat higher than those met with in practice, but they served to confirm experimentally opinions previously held by cement manufacturers.

While there is no definite information to that effect it is generally accepted as a fact that the presence of alkalies lower the temperature at which clinkering takes place. In a small furnace which the writer had he could never quite get the temperature up to the point for a thorough burning of the Lehigh cement-rock limestone mixtures, but if the small cubes of powdered material were made up with water containing enough sodium carbonate to make the mixture analyze about 1.5 per cent soda, the clinkering could easily be accomplished.

Iron always plays an important part in aiding the clinkering. The white Portland cements at present on the market are all hard to burn. Fluorspar or calcium fluoride, CaF_2, has also the effect of lowering the clinkering temperature and has been used, commercially, for that purpose, I believe.

Thermo—Chemistry of Burning

Referring to the two major operations performed in the kiln, namely (1) the decomposition of the carbonates of calcium and magnesium into the oxides of these metals, lime and magnesia, and (2) the recombination of these oxides with silica and alumina

[1] *J. Am. Chem. Soc.*, XXIV, p. 969, and XXV, p. 1103.

[2] *J. Am. Chem. Soc.*, XXIV, p. 248.

to form the di- and tricalcium silicates, and tricalcium aluminate, we have two separate and distinct kinds of thermal reaction. The first reaction, the decomposition of the carbonates, is an *endothermic* reaction, that is, it requires heat to bring it about. The second reaction, the formation of the silicates is *exothermic*, or a heat producing reaction. Of the various secondary chemical changes which occur in the kiln, some are exothermic and some are endothermic. The evaporation of the water whether this be free as in slurry or combined as in dried clay requires heat. The oxidation of the iron and the burning of the sulphur, carbon and other organic matter are exothermic or heat producing.

If a quantity of cement raw material is placed in a crucible and a pyrometer is inserted well into this and then heat is applied to the crucible at a uniform rate, it will be found that the temperature will rise quite rapidly up to about 1,650° F. When this point is reached, the temperature remains stationary for a little while and then begins to rise again. In other words, when we first apply heat to the crucible all of this is utilized to raise the temperature of the mix until that temperature (1,650°) is reached at which the carbonates begin to decompose. After this, for a while, all of the heat which is supplied to the material is utilized in decomposing the carbonates into lime and magnesia. When the decomposition is complete, the effect of the heat is again to raise the temperature of the material gradually until the point (approximately 2,435° F.) is reached, where the lime combines with the silica and alumina when the temperature will begin to increase very much more rapidly. This more rapid increase is due to the additional heat which is supplied by the second reaction or the forming of the silicates and aluminates of lime. The diagram given as Fig. 90 illustrates this.

The quantity of heat generated by chemical reaction or required to bring it about is usually expressed in terms of one of two units. These are the British thermal unit, usually abbreviated to B. t. u. and the Calorie sometimes abbreviated to Cal. The British thermal unit is the heat required to raise the temperature of one pound of pure water through 1° F. at or near 39.1° F., the temperature of its maximum density. The calorie is the heat

necessary to raise the temperature of one kilogram of water from 4° C. to 5° C. A calorie[1] is equivalent to 3.968 B. t. u., and a B. t. u. to 0.252 calorie. The B. t. u., however, produced by the oxidation or combustion of one pound of a substance is 9/5 of the number of calories which would be produced by one kilogram

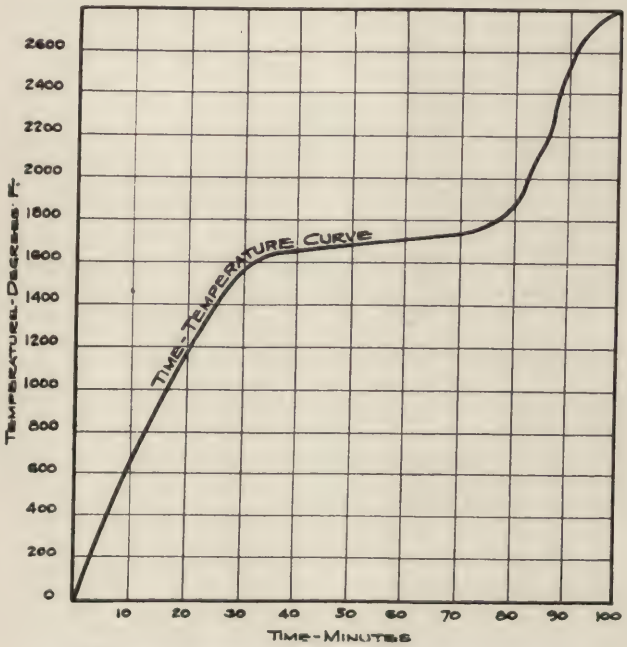


Fig. 90.—Diagram showing time-temperature curve in clinkering cement raw materials.

of the substance. Hence, to reduce calories per kilogram to B. t. u. per pound multiply by 9/5 (or 1.8) while to change B. t. u. per pound to calories per kilogram multiply by 5/9.

The heat of the formation of a chemical compound is usually expressed in terms of the molecular weight of the substances combined and of the products formed. Thus the heat produced by the burning of carbon to carbon dioxide is 97,200 cal. which

[1] The gram-calorie is expressed as the heat necessary to raise the temperature of 1 gram of water 1° C. Gram-calories per gram are of course equivalent to calories per kilogram, but the gram-calorie itself is equivalent to 0.001 calorie.

means that when 12 kilograms of carbon are burned with 32 kilograms of oxygen forming 44 kilograms of carbon dioxide, 97,200 cal. are produced. This is, of course, equivalent to 8,100 cal. per kilogram of carbon burned or to 2,209 cal. per kilogram of carbon dioxide formed. The former figure is, of course, equivalent to 14,580 B. t. u. per pound of carbon burned.

Heat of Decomposition

The heat necessary to decompose the carbonates has been determined with a fair degree of accuracy by Berthelot and others. Berthelot places the figure for the decomposition of calcium carbonate into calcium oxide and carbon dioxide at 43,300 cals., Thomsen at 42,520 cals. and De Forcrand[1] at 43,300 cals. The latter figure is probably quite near the truth and is equivalent to 779 B. t. u. per pound of calcium carbonate decomposed or 1,392 B. t. u. per pound of lime formed. De Forcrand[2] places the molecular heat of formation of magnesium oxide from the carbonate at 28,900 cal. and Simek at 23,200. The former figure is generally accepted and this is equivalent to 619 B. t. u. per pound of magnesium carbonate decomposed or 1,282 B. t. u. per pound of magnesia formed.

These reactions occur at a definite temperature for each pressure and will not occur until this temperature is reached. This temperature is known as the *dissociation temperature.* The figures most accepted are those of Mitchell[3] who placed the dissociation of calcium carbonate into lime and carbon dioxide at 896° C. at 760 millimeters pressure. This is equivalent to 1,645° F. at 29.92 inches barometric pressure. The same authority places the dissociation temperature of magnesium carbonate at 756° C. at 760 millimeters pressure. This is equivalent to 1,361° F. at 29.92 inches barometric pressure. The dissociation temperature decreases in both cases as the pressure decreases and visa versa increases with the pressure.

[1] De Forcrand, *Comptes Rendus,* Vol. CXLVI, p. 511 (1908).

[2] De Forcrand, *Ibid.*

[3] Mitchell, *J. Chem. Soc.,* Vol. CXXIII, p. 1055 (1923).

The heat necessary to evaporate free water is 970.4 B. t. u. per pound of water and to drive off combined water 1,100 B. t. u. per pound.

The Heat of Formation of Clinker

The heat liberated by the formation of the clinker from the oxides is variously placed by authorities at from 180 to 828 B. t. u. per pound of clinker formed. The latter figure is much too high. Tschernobaeff made a direct measurement in 1911 of the heat formed by burning calcium carbonate and clay to clinker in a bomb calorimeter in the presence of charcoal as a heating agent. He placed the heat of formation at 240 B. t. u. per pound of clinker formed as the result of this. Mr. W. S. Landis also determined the heat of formation of clinker in a like manner. His determination gave 200 B. t. u. per pound of clinker formed. R. Nacken, in 1922, determined the heat formed by solution of the materials in hydrochloric and hydrofluoric acid and measuring the heat of solution and other thermal changes. He placed the heat of formation of clinker at 180 B. t. u. per pound. In 1914, O. Dormann calculated the heat of formation from the best available data (Tschernobaeff's) on the heat of formation of the calcium silicates and aluminates. He gave the figure as 201 to 203 B. t. u. per pound. A somewhat later calculation by R. Coghlan employing methods similar to Dormann placed the figure at 178 B. t. u. per pound. Thus we have three figures obtained by experimental methods and two by carefully made calculations from the best available data on the heat of formation of the calcium silicates and aluminates which range from 178 to 240 B. t. u. per pound of clinker formed. The author now employs Landis's figure, or 200 B. t. u. per pound of clinker formed.

Various determinations of the specific heat of the materials employed in cement manufacture have been made—most of them are for low temperatures only, however. The most acceptable figures are

	Mean specific heat
Cement clinker 2,000°–0°	0.246
Calcium carbonate 0°–300°	0.22

Magnesium carbonate 24°–100°	0.20
Clay 20°–98°	0.22

The latter three figures are probably at least 0.02 to 0.05 too low between the temperature of the air and that of dissociation. The author has usually employed the figure 0.25 as the mean specific heat of cement raw material between zero and dissociation temperature.

Table XXVI gives in convenient form the heats of the various reactions in cement burning.

TABLE XXVI.—Heat of Various Reactions in Cement Burning

	B t u.
1 Lb. of carbon (C) burned to CO_2 gives off	14,540
1 Lb. of sulphur (S) burned to SO_2 gives off	4,050
1 Lb. of hydrogen (H) burned to H_2O gives off	54,500
1 Lb. of calcium carbonate ($CaCO_3$) decomposed into CaO and CO_2 requires	779
1 Lb. of magnesium carbonate ($MgCO_3$) decomposed into MgO and CO_2 requires	619
1 Lb. of calcium oxide (CaO) formed from $CaCO_3$ requires	1,392
1 Lb. of magnesium oxide (MgO) formed from MgCO, requires	1,282
1 Lb. of clinker formed gives off	200
1 Lb. of raw material (free of CO_2) burned to clinker gives off	127
1 Lb. of combined water requires for its liberation	1,100

Heat Required to Burn Cement

The actual heat required to burn cement is, of course, the balance between the endothermic and the exothermic reactions given previously. In other words: assuming a raw material of the following composition:

Silica	14.0
Alumina and ferric oxide	6.7
Calcium carbonate	74.8
Magnesium carbonate	1.2
Combined water	0.6
Miscellaneous	2.7
	100.0

One hundred pounds of the above raw material will produce about 64 pounds of clinker if burned with oil or 1.55 pounds of raw material will be required for one pound of clinker.

Neglecting minor reactions, the heat necessary to form clinker from the above raw material will then be found as follows:

ENDOTHERMIC REACTIONS

	B. t. u.
Heat required for decomposition of the carbonates	
(CaO, CO_2) $1.55 \times 0.748 \times 779$	903
(MgO, CO_2) $1.55 \times 0.012 \times 619$	12
Total endothermic reactions	915

EXOTHERMIC REACTION

Heat liberated by formation of clinker 1×200	200
Total exothermic reaction	200

BALANCE

Endothermic reactions	915
Exothermic reactions	200
Balance to be supplied by fuel	715

In a wet process plant, there must be supplied an additional amount of heat—enough to evaporate the water from the slurry. Assuming the slurry to contain 40 per cent water and 1.55 pounds dry material required for 1 pound clinker the additional items are:

ENDOTHERMIC REACTION

Water — $1.55 : x :: 60 : 40$, $x = 1.04$.

Evaporating 1.04 lbs. of water at and from 212° F. — $1.04 \times 970 = 1{,}009$

The above supposes the water evaporated to be cooled to the starting temperature but not condensed.

We thus see that to produce cement from dry raw materials requires 715 B. t. u. per pound of cement and from slurry containing 40 per cent water, 1,724 B. t. u. The wet process increases the work to be done by the kiln by about 140 per cent.

Assuming that there are 376 pounds of clinker in a barrel of cement, the heat theoretically required to burn the latter by the dry process is 715×376 or 268,840 B. t. u. This is equivalent to about 19 pounds of good bituminous coal (14,000 B. t. u. to the pound). The average amount of such fuel actually required in practice ranges from 80 to 100 pounds which makes the efficiency of the rotary kiln burning dry materials 20 to 25 per

cent. In the wet process the heat requirements are 648,224 B. t. u. per barrel, equivalent to 46 pounds coal, and the fuel actually used ranges from 115 to 140 pounds. The efficiency of the kiln burning wet is, therefore, from 34 to 41 per cent. This seems to bear out the contention that kilns burn slurry more efficiently than dry mix.

The amount of heat theoretically required to evaporate the water in slurry ranges from 300,000 to 400,000 B. t. u. per barrel. This is equivalent to from 21 to 29 pounds of coal (14,000 B. t. u. per pound). This figure supposes water cooled but not condensed.

The figure 29 pounds of coal per barrel is an ideal one, and in order to realize it in practice we would have to recover all the heat not actually utilized in the chemical reaction. We would have to cut off all radiation from the kiln, and the clinker and the flue gases would have to leave the kiln at the temperature of the air.

Of course, it is impossible to do this economically. There will always be some loss by radiation. We must also have sufficient difference between the temperature of the waste gases and the outside air to produce natural draft.

Application of Heat

In a cement kiln, our object is to apply heat in the fuel to decompose the limestone. This is done by burning the fuel and passing the products of combustion over a body of the cement raw material. The fore part of the kiln acts as a combustion chamber. The transferring of heat takes place from the gases to the cement mix and to the walls of the kiln, the heat being transformed from the latter again to the mix so that the mix is heated in two ways—chiefly by the products of combustion directly and to a less extent through the walls of the kiln.

The first step in the burning of clinker is, of course, the source of heat. Pulverized coal or oil are used almost universally.[1] Fortunately in both these fuels we have material which is sus-

[1] The various fuels employed and methods of preparation and use are described in detail in the next chapter.

ceptible to very nice regulation and which can be burned with practically the exact amount of air theoretically necessary for combustion. We do not, as is the case with grate and stoker firing, have to consider the condition of the fuel body, etc., with reference to supplying the oxygen to burn the fuel. Nor do we have to consider carbon or unconsumed coal carried out by the ash. Analyses of kiln gases show that in the great majority of cases the coal is burned either with a slight deficiency (a reducing flame) or with a very small excess of air (an oxidizing flame). In other words with practically the theoretical amount of oxygen necessary (a neutral flame).

Fortunately in a cement kiln we do not as in metallurgical furnaces have to consider the chemical qualities of the flame, and so far as the essential chemical combinations and decompositions to be effected in this are concerned these take place equally well in a reducing or an oxidizing atmosphere, consequently our concern is chiefly towards burning the fuel efficiently and in such a manner that its heat energy may be most effectively utilized.

The greatest factor in determining the temperature of the flame is the amount of air used for combustion, thus if we burn one pound of coal with just the quantity of air necessary for combustion, the gases produced would weigh about 11 pounds. If we use twice as much air as necessary the products will weigh 21 pounds. Manifestly if we transfer the heat of one pound of coal to 11 pounds of gas the temperature of the latter will be much higher than if we transfer the same quantity of heat to 21 pounds of gas.

The temperature of the flame unquestionably has a great influence on both the economy and the chemistry of cement burning. Aside from the fact that with higher temperatures in the kiln less time is required for burning or a coarser raw material may be used, it is well known that the rate of heat transfer is proportional to the difference between the gases and the material to be heated, other conditions remaining constant; hence the higher the flame temperature the more rapidly the heat can be transferred to the mixture.

There is another objection to excess air. Some heat is always carried away by the gases leaving the kiln. This heat is proportional to the quantity and temperature of the gases. Eleven pounds of gas leaving the kiln will carry off only about half the heat which will be carried off by 21 pounds. This applies whether we use waste heat boilers or not and the relative percentage of heat carried off by the gases will be the same whether they are at a low or high temperature—that is to say, at the same temperature 11 pounds of gas will carry off only half as much heat as 21 pounds, whether the temperature of the exhaust gases be 400° F. or 1,600° F.

Air Required for Combustion

The air required for combustion is found from the ultimate analysis of the fuel. In order to illustrate the method we will assume the burning is to be done with slack coal of the following composition.

Water (110° C.)	1.9
Carbon	74.9
Hydrogen	4.8
Oxygen	8.6
Nitrogen	1.4
Sulphur	0.7
Ash	7.7
	100.0

Neglecting the sulphur which is present in very small amount the combustible elements in 100 pounds of this coal are 74.9 pounds of carbon and 4.8 pounds of hydrogen. Of this hydrogen, however, $\frac{8.6}{8}$ pounds will be needed for the oxygen of the coal itself, leaving only $(4.8 - \frac{8.6}{8} = 4.8 - 1.1 = 3.7)$ to require outside oxygen; hence, to burn 100 pounds of this coal will require

For carbon, $12 : 32 :: 74.9 : x$	$x =$ 200 lbs. O
For hydrogen, $2 : 16 :: 3.7 : x$	$x =$ 30 lbs. O
For 100 lbs. of coal	230 lbs. O

Now air is 23.1 per cent (by weight) oxygen, therefore, 230 pounds of oxygen is equivalent to $230 \div 23.1 = 996$ pounds air. This is, of course, equal to 9.96 pounds of air per pound of coal.

By a similar calculation, it will be found that the air required to burn one pound of crude California oil (composition—carbon, 86 per cent; hydrogen, 11 per cent; nitrogen, 2 per cent; sulphur 1 per cent) amounts to 13.8 pounds; or for one gallon (8 pounds) of this oil 110.4 pounds of air.

Products of Combustion.

The products of combustion may also be calculated from the ultimate analysis of the fuel. Thus, referring to the analysis of coal in the preceding section, the hydrogen in 100 pounds of coal will form 43 pounds of water ($2 : 18 :: 4.8 : x, x = 43.2$). Added to the latter quantity will be the moisture in the coal (1.9 per cent or a total of 45 pounds of water produced. The carbon will form 275 pounds of carbon dioxide. ($12 : 44 :: 74.9 : x$, $x = 274.6$). The sulphur will form 1.4 pounds of sulphur dioxide ($32 : 64 :: 0.7 : x$, $x = 1.4$) We have determined in the preceding examples that 230 pounds of oxygen are needed for the combustion of 100 pounds of coal and that this is equivalent to 996 pounds of air. The nitrogen in the air will then be 996 — 230 or 766 pounds. This will be increased by the nitrogen in the coal itself (1.4 per cent) to 767 pounds. The above quantities are the products of combustion from 100 pounds of coal The products from one pound will of course be:

	Lbs.
Water	0.45
Carbon dioxide	2.75
Sulphur dioxide	0.01
Nitrogen	7.67
Total	10.88

As a check[1] on the above calculation, the total weight given above should equal the air required for combustion plus the com-

[1] A method of calculating the quantity of waste gases from the analysis of the exit gas itself is given in the section on the waste heat boiler, Chapter XV.

bustible part of the coal (100 per cent of ash), or in this case, $996 + (100 - 7.7) = 1{,}088$ pounds, for 100 pounds of coal.

Assuming that 120 pounds of coal are required to burn a barrel of cement, the products of combustion would be per barrel of cement burned:

	Lbs.
Water	54
Carbon dioxide	330
Sulphur dioxide	1
Nitrogen	920
	1,305

By a similar process of calculation, it will be found that the products from the combustion of California crude oil (C, 86 per cent; H, 11 per cent; N, 2 per cent; S, 1 per cent) amount to:

	Per pound Lbs	Per gal, Lbs.
Carbon dioxide	3.17	25.36
Water	.96	7.68
Nitrogen	10.65	85.20
Sulphur dioxide	.02	.16
Total	14.80	118.40

Excess Air Used in Burning.

The excess of air admitted to the kiln over and above that required to consume the coal has been variously stated at from 100 to 150 per cent, above the theoretical quantity. From the result of many analyses made by myself and assistants I am confident that this does not represent normal conditions. If the sample is taken from the kiln stack a large quantity of air, which has leaked in through the annular opening between the kiln and the brick-work of the flue is sure to be present, and consequently make the excess air appear much greater than it really is. The gas samples should be taken from the inside of the mouth of the kiln so that there is no air mixed with it which does not pass through the kiln. Below are given some average analyses of waste gases from kilns working under various conditions.

1. Average of all samples taken when the kiln was working normally. No flame or black smoke issuing from the kiln stack but only a thin white or reddish vapor.

Carbon dioxide	27.4
Carbon monoxide	0.3
Oxygen	2.7
Nitrogen	69.6
	100.0

2. Average of all samples taken when the kiln stacks were smoking.

Carbon dioxide	19.2
Carbon monoxide	1.2
Oxygen	3.4
Nitrogen	76.2
	100.0

3. Average of all samples taken when kiln stacks were flaming:

Carbon dioxide	14.2
Carbon monoxide	5.8
Oxygen	1.1
Nitrogen	78.9
	100.0

The nitrogen in the gases represents the air admitted for combustion as practically all of it is from either the excess air or the air actually used to burn the coal. A small part of the nitrogen comes from the coal, however, but for practical calculations the nitrogen may be considered as all coming from the air. The excess air is shown by the oxygen. If we calculate the nitrogen equivalent to this oxygen by multiplying the percentage of the latter by 3.78, the result will be the nitrogen carried in by the excess air and this nitrogen subtracted from the total percentage of nitrogen found by the analysis will give the nitrogen belonging to the air needed to support combustion, from which data the excess can be calculated. For example, to find excess air in sample:

Analysis No. 1.

	Per cent
Total nitrogen	69.6
Nitrogen in excess air 2.7 × 3.78	10.2
Nitrogen in necessary air	59.4

Ratio — 59.4 : 69.4 :: 100 : x

$x = 117$.

Excess = 17 per cent of air necessary for combustion.

The above calculation is not strictly accurate for a number of reasons, but for practical use it answers the purpose very well since we never know in mill practice under present conditions exactly how much coal we are burning, or how much carbon dioxide is being driven off at a given time from the raw material.

Of the air admitted to the kiln for combustion, part is blown in with coal; the rest enters between the hood and the kiln and where the clinker drops out, and is drawn in by the draft of the kiln.

Heat Carried Out by Waste Gases.

The chief object in calculating the weight of the products of combustion is to determine the heat carried out of the kiln by these. If we multiply the quantity of each gas present in the exit gas by the mean thermal capacity of this gas and the temperature, the product will be the heat carried out by this gas. Figure 91 gives the mean thermal capacities of the gases found in the exit gas from cement kilns. It will be noticed that this figure varies with the temperature. For example, let us suppose the exit gases are at 1,200° F. above the atmospheric temperature, then the products of combustion in the preceding example carry off heat as follows: (The small amount of sulphur dioxide may be neglected).

By water vapor	54 × 1,200 × 0.54 =	34,992 B. t. u.
By carbon dioxide	330 × 1,200 × 0.252 =	99,792 B. t. u.
By nitrogen	920 × 1,200 × 0.261 =	288,144 B. t. u.
Total		422,928 B. t. u.

If 17 per cent excess air is employed in burning this would carry off (9.96 × 120) × 0.17 × 1,200 × 0.254 = 61,930 B. t. u. per barrel of cement.

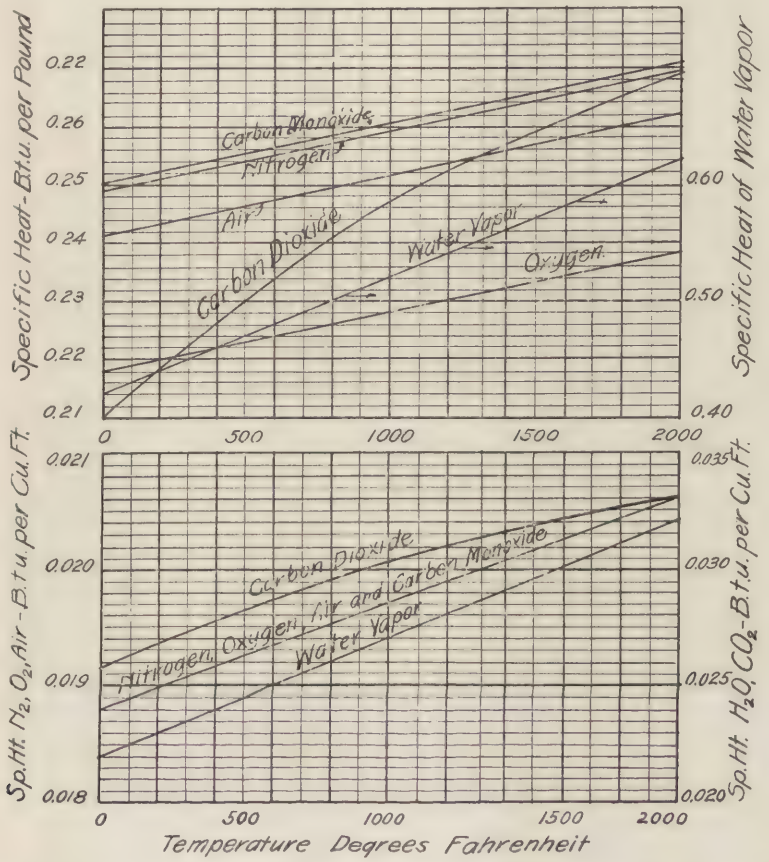


Fig. 91.—Specific heat of gases at various temperatures. Upper curves give specific heat of the gases per pound per degree F. rise. Lower curves give specific heat per cubic foot per degree F. rise.

In addition to the carbon dioxide and water formed by combustion of the fuel, there will also be the carbon dioxide and water driven off from the raw materials. The amount of this

can, of course, be determined from an analysis of the latter Assuming that 900 pounds of slurry are required to produce a barrel of cement and that 33⅓ per cent of this is water and 33⅓ per cent of the dry material is carbon dioxide the amount of heat carried out by these two gases is as follows:

The carbon dioxide from the raw material would carry off $200 \times 1{,}200 \times 0.252 = 60{,}480$ B. t. u.

Similarly the water vapor present in the exit gases would carry out $300 \times 1{,}200 \times 0.54 = 194{,}400$ B. t. u. This is in addition to the *latent* heat of evaporation.

The total sensible heat in the exit gases from the kiln per barrel of cement would then be the sum of these four quantities or

Heat in products of combustion	422,928 B. t. u.
Heat in excess air	61,930 B. t. u.
Heat in carbon dioxide from raw materials	60,480 B. t. u.
Heat in water vapor from slurry	194,400 B. t. u.
Total per barrel of cement	739,738 B. t. u.

Heat Loss Due to Carbon Burned to Carbon Monoxide.

If the gas contains carbon monoxide this carries out latent heat. That is heat which would be produced if the carbon monoxide was burned to carbon dioxide. One cubic foot of carbon monoxide will produce 334 B. t. u., one pound of carbon monoxide 4,280 B. t. u. Gas analyses are usually expressed in percentage by volume and our heat calculations have been by weight. Now one pound of carbon will produce an equal *volume* of either carbon dioxide or carbon monoxide, whichever happens to be formed, and from our previous calculations we know that of a total of 530 pounds of carbon dioxide 200 pounds or 38 per cent comes from the raw material and 330 pounds or 62 per cent from the fuel.

Hence if our gas contains 0.3 per cent carbon monoxide and 27.4 per cent carbon dioxide, of this total $27.7 \times 0.62 = 17.2$ per cent comes from the coal. Hence the relative amounts of carbon burned to carbon monoxide and carbon dioxide respectively are as 0.3 is to 17.2 or $0.3 : 17.2 :: 1.7 : 98.3$. Of our carbon therefore 98.3 per cent has been burned to carbon dioxide and 1.7

per cent to carbon monoxide. Now one pound of carbon burned to carbon monoxide will produce 4,374 B. t. u. and to carbon dioxide 14,580 B. t. u. For every pound of carbon burned to carbon monoxide there will be lost, therefore, 10,206 B. t. u. Now in 120 pounds of coal containing 74.9 per cent of carbon there will be 90 pounds of carbon. If 1.7 per cent of this is burned to carbon monoxide, the heat lost will be $90 \times 0.017 \times 10{,}206 = 15{,}615$ B. t. u. per barrel of cement.

Heat Lost by Radiation.

Radiation losses are usually figured by dividing the kiln into a number of sections and determining the temperature at the middle of each section. The area of surface exposed in each section is then determined and from this the heat loss is calculated by multiplying this area by the heat radiation per square foot of surface at the ascertained temperature. Various investigators have measured the heat lost from a heated metal wall for various temperatures. Darling's figures[1] are now most accepted. Fig. 92 shows graphically the radiation losses per square foot of surface at various temperatures and is prepared from Darling's figures. Boeck's formula[2] is also often used. It is probable that the figures obtained in either case are only approximate, as the heat radiated varies greatly under different conditions, thus it has been found that the heat lost from a horizontal surface is 22 per cent greater than that from a vertical surface and hence the loss from a cylindrical surface would lie somewhere in between these two figures. The loss from a surface exposed to wind is 30 per cent greater and of one exposed to the wind and rain 70 per cent greater than from a surface exposed only to still air. The kiln is moving which increases the radiation loss somewhat beyond what would be obtained from a stationary surface.

The measurement of the temperature of the kiln shell is by no means easy. The method usually employed is to insert thermomters into steel wells or thimbles welded to the kiln shell. The temperature of these is taken at frequent intervals or a regis-

[1] C. R. Darling, *Engineering* (London) Mar. 14, 1919, p. 643.

[2] Boeck, *Jour. Am. Soc. Mech. Engrs.*, Aug., 1916.

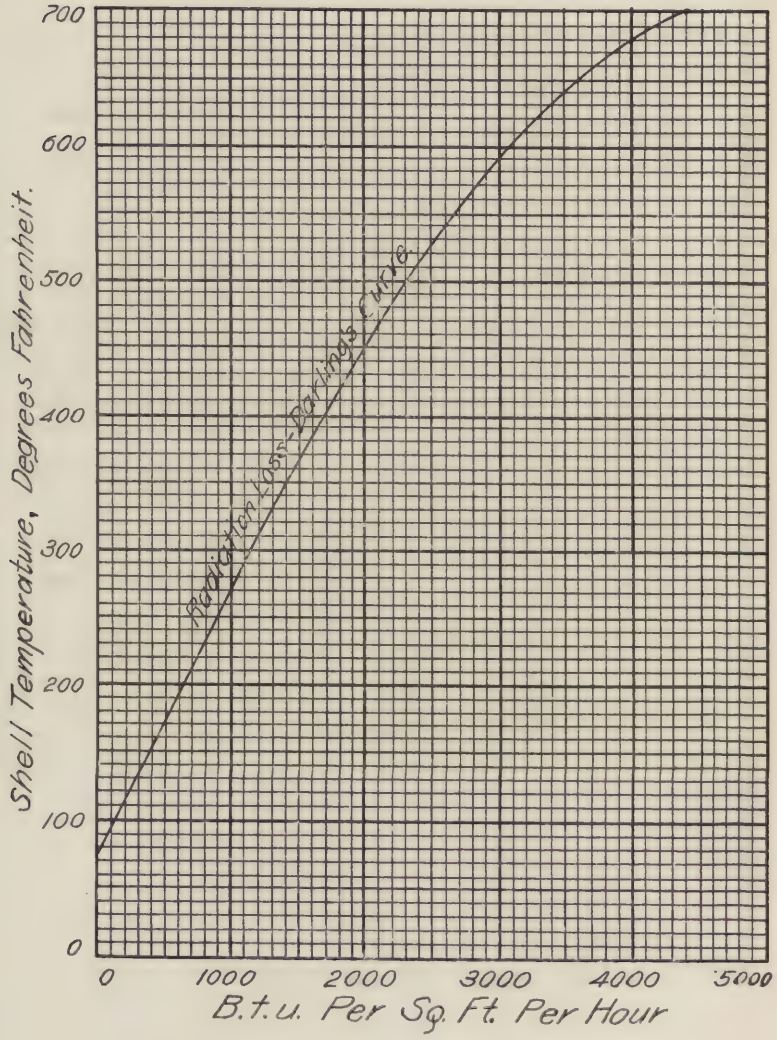


Fig. 92.—Radiation losses from the kiln shell (Darlings).

tering instrument is used. The readings are usually averaged over the period of the test.

The following example shows the heat losses from a rotary kiln, 8 feet diameter by 125 feet long, burning wet materials. The kiln was divided into three zones each 25 feet long at the feed end and into four zones each 12½ feet long at the firing end. Thermometers were inserted in the center of each zone. That is the first themometer was inserted 5 feet from the firing end, the second 15 feet, etc. The average temperature at each station, the heat lost per square foot at this temperature, the area of surface of each zone and the total heat lost per section is shown in Table XXVII. The figures in Column 5 are in each instance the product of corresponding figures in Columns 3 and 4. The figures in Column 3 are taken from Fig. 92.

The total heat lost per hour in this instance was 3,906,640 B. t. u. The output of the kiln during the test was 530 barrels per day or 22.1 barrels per hour. The heat lost per barrel by radiation was, therefore, 176,771 B. t. u. The fuel required per barrel was 120 pounds of coal (14,000 B. t. u.) equivalent to 1,680,000 B. t. u. The heat by radiation in this instance therefore was equivalent to 10.5 per cent of the fuel.

TABLE XXVII.—Heat Lost by Radiation from Rotary Kiln 8 Feet Diameter × 125 Feet Long Burning Wet Materials

Zone	Average temperature °F.	Heat lost per sq. ft. of zone per hour—B. t. u.	Area of zone Sq. ft.	Heat lost per zone B. t. u.
1	330	1,300	314	308,200
2	360	1,500	314	439,600
3	340	1,400	314	471,000
4	320	1,260	314	395,640
5	315	1,250	628	785,000
6	313	1,250	628	785,000
7	300	1,150	628	722,200
	Total			3,906,640

Heat Balance.

In calculating the efficiency, etc., of a rotary cement kiln, what is known as a heat balance is often made. That is the heat received from the combustion of the fuel, the formation of clinker

etc., is compared with the heat expended in decomposing the carbonates of lime and magnesia—or lost in various ways. The two sums should, of course, balance.

The chief items making up this heat balance are:

Plus Items.

1. Heat derived from the combustion of the fuel.
2. Heat liberated by the formation of the clinker.
3. Heat brought in by the air used for combustion.
4. Heat brought in by the fuel.
5. Heat brought in by the raw materials.

Negative Items.

6. Heat utilized in decomposing carbonate of lime.
7. Heat utilized in decomposing carbonate of magnesia.
8. Heat utilized in evaporating water.
9. Heat carried out by the clinker.
10. Heat carried out by the stack-gases.
11. Heat lost by incomplete combustion (C to CO).
12. Heat lost by radiation.

The following examples will show how the various items are calculated and the balance is struck.

1. The heat liberated by the fuel may be determined directly in a calorimeter or calculated from the analysis. For methods of determining this the reader is referred to any of the standard works on analytical chemistry or the chemistry of fuels[1].

Let us suppose we find the coal has a fuel value of 14,000 B. t. u. per pound and that 120 pounds are required to burn a barrel of cement. Then the heat supplied by the fuel is 1,680,000 B. t. u. per barrel of clinker.

2. The method of calculating the heat of the formation of the clinker has been shown previously. If the calculation is on the "per barrel" basis it is, of course, 200 × 376 or 75,200 B. t. u.

[1] Meade, "The Chemists' Pocket Manual;" Somermeier, "Coal; Its Composition, Analysis, Utilization and Valuation"; Stillman, "Engineering Chemistry"; Gill, "Gas and Fuel Analysis for Beginners," etc.

3. In order to find the heat brought in by the air it is necessary to know (1) the weight of air required for combustion. (2) The temperature of this air. (3) The excess air employed and (4) The specific heat of air.

The method of determining excess air has already been explained. If this is found to be 17 per cent of that theoretically necessary, the total amount of air used to burn one pound of coal would be $9.96 \times 1.17 = 11.65$ pounds. If we burn 120 pounds of coal per barrel, the air employed for this is 1,398 pounds.

Again suppose the temperature of the air is at 92° F. and we have decided to make 32° F. our base. The mean thermal capacity of air (32° — 90° F.) is 0.242. The heat brought in by the air is then $60 \times 0.242 \times 1{,}398$ or 20,299 B. t. u. per barrel.

4. The sensible heat brought in by the fuel is always small. Assume the coal to be at 92° F. and its specific heat 0.24, the heat brought in is then $120\ (92 - 32) \times 0.24 = 1{,}728$ B. t. u. per barrel.

5. The heat brought in by the raw material is, of course, the sum of that brought in by the solid matter and the water. Let us assume 900 pounds of slurry containing 33⅓ per cent of water at a temperature of 97° F. are used per barrel. Then the slurry will contain 300 pounds of water and 600 pounds of solids and the heat brought in will be

In solids, $600 \times (97 - 32) \times 0.22 =$	9,580 B. t. u.
In water, $300 \times (97 - 32) \times 1.00 =$	19,500 B. t. u.
Total heat brought in by the slurry	28,080 B. t. u.

6. The heat utilized in decomposing carbonate of lime is calculated as previously explained. If the raw material contains 41 per cent lime, then the heat required will be $600 \times 0.41 \times 1{,}392 = 342{,}432$ B. t. u.

7. Similarly if the raw material contains 2 per cent magnesium carbonate the heat required to decompose this will be $600 \times 0.02 \times 1{,}282 = 15{,}384$ B. t. u.

8. The heat utilized in evaporating water will be first the heat necessary to raise the temperature of the water from 32° to 212° F. and then the latent heat of evaporation, or

To raise temperature one pound water from	
32 to 212° F. (212 — 32) × 1	180 B. t. u.
Latent heat of evaporation	970 B. t. u.
Total heat per pound of water	1,150 B. t. u.
Heat for 300 pounds of water	345,000 B. t. u.

9. The heat carried out by the clinker is found by multiplying the mean specific heat of the clinker by its temperature. The specific heat of clinker is 0.246 and let us suppose its temperature to be 2,032° F. The heat lost is then, 376 × (2,032 — 32) × 0.0246 = 184,992 B. t. u.

10. Let us assume the conditions given on page 300. The heat carried out by the waste gases will then be 739,738 B. t. u. per barrel as calculated previously.

11. The method of calculating the loss of heat due to incomplete combustion of carbon has been previously explained. If the conditions are as stated in this example the heat lost due to this cause is 15,615 B. t. u. per barrel as calculated there.

12. The method of calculating the heat lost due to radiation has been explained previously and in the example given was found to be 176,771 B. t. u. per barrel.

The heat balance would then assume this form.

	Plus items	B. t. u.	B. t. u.
1.	Heat from fuel	1,680,000	
2.	Heat from formation of clinker	75,200	
3.	Heat brought in by air	20,299	
4.	Heat brought in by fuel	1,728	
5.	Heat brought in by raw materials	28,080	
	Miscellaneous and unaccounted for	14,625	1,819,932
	Negative items		
6.	Heat for decomposing $CaCO_3$	342,432	
7.	Heat for decomposing $MgCO_3$	15,384	
8.	Heat for evaporating water	345,000	
9.	Heat lost in clinker	184,992	
10.	Heat lost in stack gases	739,738	
11.	Heat lost by incomplete combustion	15,615	
12.	Heat lost by radiation	176,771	1,819,932

From the above and similar tests it is found that the heat distribution in burning cement is about as follows:

	Dry process Per cent	Wet process Per cent
For chemical reactions in burning	20	16
For evaporating water	—	19
Carried out by clinker	13	11
Carried out by stack gases	55	44
Lost by radiation	12	10
	100	100

Dust Losses

The dust losses from the rotary kiln amount to from 3 to 6 per cent of the raw material. This dust consists of coal ashes, unburned raw material, partially calcined material and certain volatile products which are driven out of the clinker and which condense either in the upper part of the kiln, in the stack or when the open air is reached (either in their original form or in new combinations) such as potash, soda and sulphate of calcium, etc. The analyses given below will give an idea of the composition of the dust. These samples were collected by electrical precipitation.

Composition of Cement Kiln Stack Dust.

	Kiln fired with coal	Kiln fired with oil
Calcium carbonate	25.56	31.40
Calcium sulphate	7.82	6.31
Calcium oxide	18.69	19.03
Magnesium oxide	1.50	0.60
Potassium oxide—water soluble	9.58	14.15
Potassium oxide—insoluble	3.72	1.26
Sodium oxide—water soluble	1.07	8.37
Sodium oxide—insoluble	0.95	none
Silica	16.80	8.41
Iron oxide and alumina	9.06	7.02
Undetermined	3.45	5.25
	100.00	100.00

The dust losses depend to some extent on the plant but it is safe to say that even under the most favorable conditions where dust precipitation apparatus is not used the loss amounts to 4 or 5 per cent on an average.

It has been frequently stated that the dust from the kiln stacks of the wet process is neglible and this is held as a strong argument in favor of the wet process. The writer's study of the dust from the kiln stacks in connection with the recovery of potash, however, has led him to believe that the dust from the wet process kilns is nearly, if not actually, as great as that from the dry process.

J. G. Dean in an article in *Chemical and Metallurgical Engineering,* describing the process of recovering potash which was employed at Victorville, Cal., stated that the amount of dust collected in their dry dust flue amounted to 3 per cent of the total dry material entering the kiln and admitted this was only a portion of the dust lost because when they put in their potash system they obtained a large additional amount in the spray chamber and condenser. Results there indicated that the dust lost must have amounted to about 5 per cent of the raw material. This agrees quite closely with the dust losses of the dry process.

While the claim of less dust is generally made for the wet process, there does not seem to be available the results of any dust determination in support of this theory. Obviously it would be a comparatively easy matter to determine the dust losses by means of dust filters.

The writer cannot find any evidence that it takes less raw material to make a barrel of cement by the wet process than by the dry. The dust losses at the average dry process plant are about 5 per cent of the raw material, or about 30 pounds per barrel of cement. Obviously if the wet process saved this loss, it should certainly be indicated by the smaller quantity of raw material required to produce a barrel of cement.

Should the wet process produce less stack dust than the dry? So long as the raw materials are damp no dust would theoretically be produced, but, manifestly, the raw materials do not remain damp until they clinker. On the other hand, they are probably for the greater portion of their time in the kiln in a condition where they will dust fully as freely as with the dry process. In some chemical work undertaken by the writer in which the effort

was made to dry a very fine marl, it was found that in spite of the fact that the latter was fed into the kiln containing 60 per cent moisture, the dust losses were so great that the process could not be employed.

Examination of any sample of stack dust will show this to contain some material which has been calcined (not necessarily clinkered), some uncalcined material and some coal ash. Generally speaking, fully half and often as much as 80 per cent of the dust is material which has been fully calcined to lime (or to the extent where the limestone has been freed from carbon dioxide). It would certainly seem evident that this portion of the dust had been picked up by the rapidly moving gases after the material reached the zone where the carbon dioxide was liberated and, of course, some distance beyond the point where wet materials would have become dry.

If the slurry when it dried out, took the form of small nodules free from dust and baked sufficiently hard to prevent dusting by attrition, then there would be some reason for assuming that the wet process would not produce dust. As a matter of fact, as anyone can prove by entering a wet process kiln which has been shut down, the material dries in the form of soft nodules and dust. The nodules can be easily pulverized by rubbing between the fingers or by rolling over one another. When burned to the point where calcium oxide is formed they usually break down still further. Certainly the slight difference in appearance of the material, after this has reached that part of the kiln where carbon dioxide is being liberated, fails to warrant the statement, that one will be carried out by the gases and the other not.

Experiments made at various times show that in the dry process about half of the coal ash enters the cement and half is blown out of the kiln. The coal ash thus contributes something to the dust, usually to the amount of about 5 to 7 pounds of dust per barrel of clinker.

The supposition that the dust will be caught and precipitated by the vapor given off by the mix in drying is, of course, unfounded. The temperature of the exit gases from even a wet

kiln is far above the condensation point of steam. At such a temperature, steam is a perfect gas having the properties of any other gas and its addition to the products of combustion and the carbon dioxide might even increase the dust carrying properties of the waste gases by increasing their volume and consequently their velocity.

The idea may hold that the wet material itself will catch and retain the dust. This can occur only to a very limited extent. The slurry so long as it is damp will no doubt collect any dust which *impinges* on it, but the amount of dust which actually strikes the wet material is, of course, but a small part of the dust in the gases. Any one who has tried to wash kiln gases with water sprays will realize how thoroughly this spraying must be done in order to collect even any considerable portion of the dust.

In view of both practical data and theoretical consideration, therefore, the statement that the "wet process *elim'nates* dust" *is not warranted.*

Dust Collection

Two methods of dust collection from the kiln are in use (1) the Cottrell or Electrical Method, and (2) Washing the gases with water.

The Cottrell or electrical method of collecting dust was first proposed many years ago by Sir Oliver Lodge, the distinguished English physicist. No successful apparatus, however, was devised until Dr. Cottrell, then of the University of California, undertook to apply this principle to the precipitation of fume from smelter gases and a little later on to the precipitation of the dust from cement kiln gases. The latter undertaking was first brought to a successful conclusion at the plant of the Riverside Portland Cement Co.

Various types of apparatus for carrying out the process have been tried at different times. The first large installation at Riverside consisted of horizontal or plate treaters, but all of the later installations at cement plants employ the vertical or pipe treater. This latter consists essentially of an iron wire passing through

the center of a sheet iron pipe. These two form the electrodes and are operated by a direct current of 45,000 to 80,000 volts. The gases pass up through the tube. There is a silent discharge of electricity passing from the wire to the tube and this effects the precipitation of the dust, the larger portion of which collects on the surface of the tube.

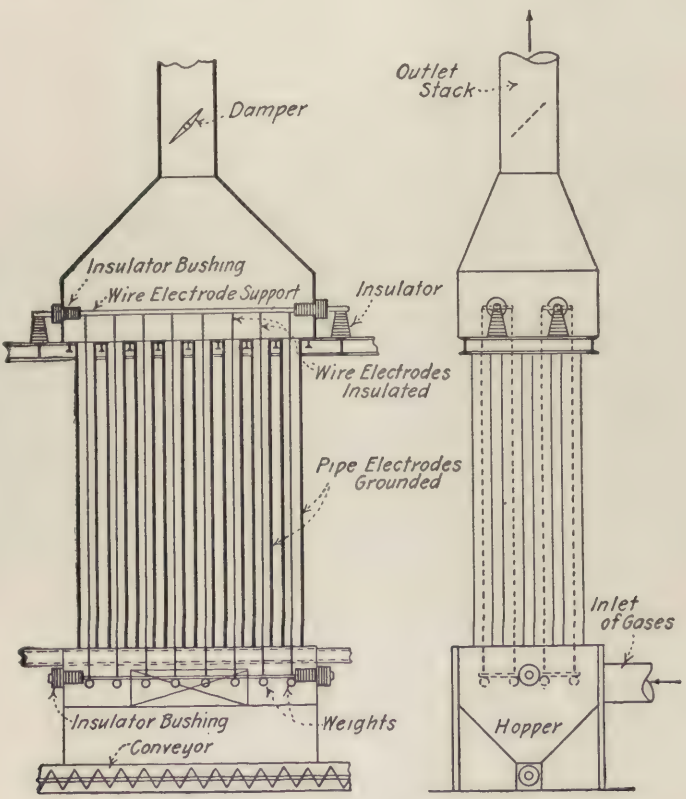


Fig. 93.—Diagram illustrating typical Cottrell dust precipitator.

Dr. Cottrell thus explains this action: "If a needle-point connected to one side of a high potential direct-current line be brought opposite to a point connected to the other side of the line, the space between them and any insulated body becomes

highly charged with electricity of the same sign as the needle, whether positive or negative; and such body if free to move will be attracted to the plate of opposite sign." In the tube treater the wire represents the needle and the surface of the tube the plate.

As installed in the cement industry, the apparatus or "treater," consists of a large number of such tubes which are connected above and below with flues. The gases enter the bottom flue and pass up through the tubes of the upper flue, or vice versa as occasion warrants. At frequent intervals, the current is interrupted

Fig. 94.—Cattrell precipitator and flue connecting this with the kilns—Clinchfield Portland Cement Co., Kingsport, Tenn.

and the dust is rapped from the surface of the tubes by means of a system of hammers. The wires are also provided with a knocking arrangement by means of which any dust which collects on them is shaken off. The dust falls into hoppers situated below the flue and from this it is drawn out as desired by means of slides and gates. A fan is generally employed to draw the gases through the treater and produce the draft in the kiln. A treater is usually divided into a number of units so that the operation of the system is not interfered with when the dust is shaken down or when repairs are made. Refer to Figures 93 and 94.

Collection by Washing the Gases with Water

The collection of dust by means of water sprays was one of the earliest methods and such methods of gas washing have been extensively employed in metallurgical and chemical industries. The cleaning of blast furnace gases by the use of water sprays is quite general in the iron industry, and in many chemical processes gases are passed through chambers in which sprays are located to free them from dust and impurities.

A number of early experimenters undertook to wash the dust out of the rotary kiln gases with water but for the most part employed too little water and passed the gases through the apparatus at too high a velocity for good results, so that all efforts were a failure until the successful installation of such a process, designed along sound engineering lines, at the plant of the California Portland Cement Co., at Colton, Cal. This installation differs from most of the recent water spray systems, however, in that the wet scrubbers are preceded by a large dry settling chamber in which the major portion of the dust is precipitated, while in the newer wet collection systems only a scrubber is used.

The first successful system installed in the cement industry was put in operation in 1911 and was the invention of T. J. Fleming, secretary and general manager of the California Portland Cement Co.[1]

The installation at Colton treats gases from rotary kilns using the dry process and from the dryers—all employing oil for fuel. The draft of the kilns and dryers is produced by fans sucking at the end of separate flues. (See Fig. 95). There is a fan, motor and flue for each kiln, but the gases from a number of kilns and the dryer are passed into one treater. The fans are operated by variable speed motors so that the draft of the kilns can be increased or diminished to suit conditions. The treater itself consists of a large rectangular chamber built of steel and reinforced concrete and divided into two sections, one a dry

[1] W. C. Hanna, *Concrete Mill Section*, Vol. XII, p. 33, also *Trans. Amer. Inst. Chem. Engrs.*, Vol. VIII, p. 65.

T. J. Flemming, *Engineering Record*, Vol. LXIX, p. 640.

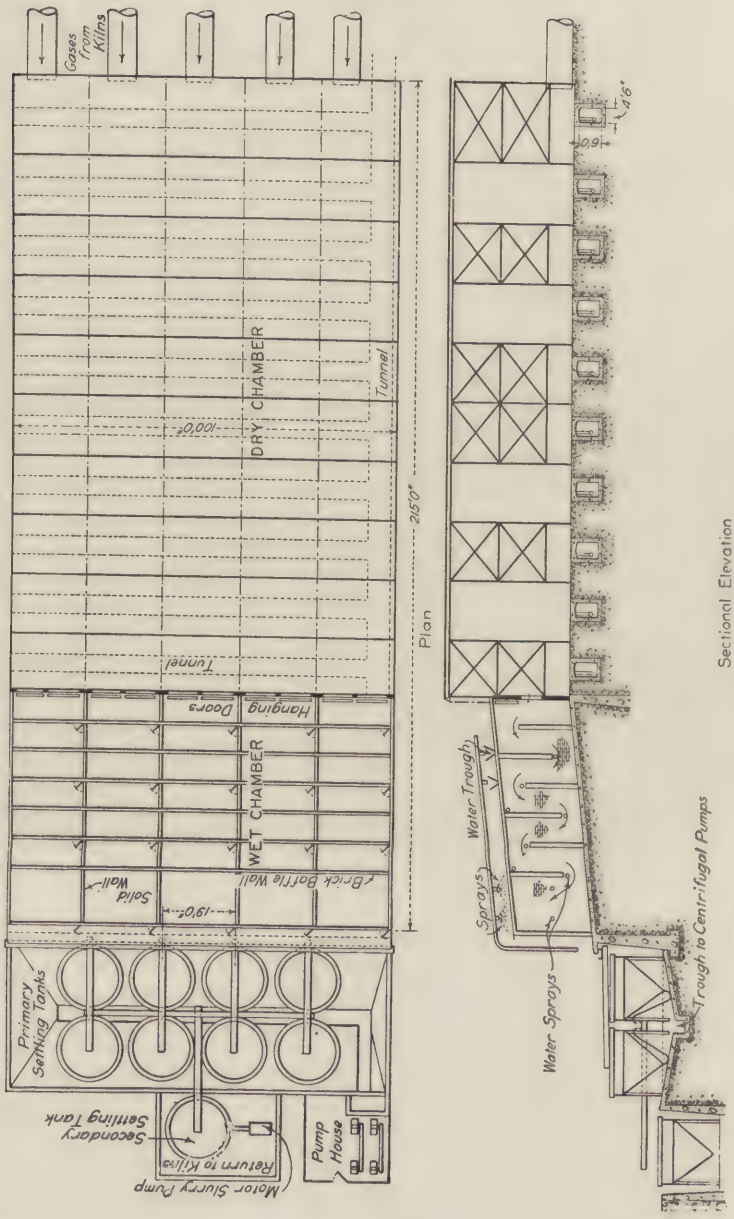


Fig. 95.—Flemming dust collection system—California Portland Cement Co., Colton, Cal.

chamber 155 feet long, 100 feet wide and 31 feet high and the other a wet chamber 60 feet long and 100 feet wide.

The fans discharge the gases from the kilns into the dry dust settling chamber in which the velocity of the gases is reduced about 90 to 95 per cent, resulting in a large amount of dust being deposited here. The extremely fine dust which does not settle in the dry chamber and the gases are then passed over to the washing chamber where the gases are forced up and down several times by means of a system of baffle-walls, causing them to follow a serpentine course. The wet chamber is provided with water sprays so as to thoroughly wash the gas. The dust settling in the dry chamber is carried out of the latter by means of screw conveyors running underneath this and the dust settling in the wet chamber is, of course, washed out of the latter by means of the water.

The water carrying the dust in suspension and forming a very thin slurry flows from the washing chambers into conical bottomed settling tanks, where the dust is allowed to settle out, and the solution is circulated through the sprays until of the desired strength after which the potash is separated out by evaporation.

Other systems for precipitating dust were chiefly connected with the recovery of potash. Such systems were installed in the plants of the Santa Cruz Portland Cement Co.,[1] The Southwestern Portland Cement Co.,[2] the Pacific Portland Cement Co., Ogden Portland Cement Co., the Utah Portland Cement Co.,[3] and the Atlas Portland Cement Co., at Hudson, N. Y.

Potash from the Cement Industry[4]

Reference has been made to the experiments by the writer and Dr. Hillebrand showing the volitilization of potash in the cement kiln. Mr. Clifford Richardson[5] read a paper at the 1904

[1] C. Krarup, *Chem. and Metl. Eng.*, Vol. XXV, p. 316.

[2] J. G. Dean, *Chem. and Metl. Eng.*, Vol. XIX, p. 439.

[3] R. K. Meade, *Rock Products*, July 17 and 31, Aug. 14 and 28, 1918.

[4] Those who are interested in this subject are referred to a series of articles by the author in *Rock Products*, July 17 and 31, August 14 and 28, 1918.

[5] Richardson, *Trans. Am. Soc. Test. Matls.*, Vol. IV, p. 465.

meeting of the American Society for Testing Materials in which he proposed to the cement industry that they collect the potash lost, by means of a water spray and stated that Dr. Hillebrand had applied for a patent upon such a process. However, no patent was ever granted. The matter was discussed informally but it was generally conceded at that time that the cost of collecting this dust with the apparatus then known of, namely water sprays, would far exceed its value, if indeed it could be collected at all.

The question of collecting potash from the cement industry, received no further consideration until imports of potash from Germany were discontinued by the World war in 1914.

Due to agitation against the dust, two plants in Southern California had made provision to collect this and with the dust they also collected considerable potash mixed with the latter. The plant of the Riverside Portland Cement Co., employed the Cottrell System[1] of dust collection, while the plant of the California Portland Cement Co. employed a system[2] devised by Mr. T. J. Fleming.

In order to obtain a material richer in potash, all of this dust was fed to a supplementary kiln and was burned to cement in that kiln. From this kiln, dust was obtained running in excess of 30 per cent K_2O, but it was found that most of the potash in the dust fed into the kilns did not volatilize but remained with the clinker, due no doubt to the fact that the potash was present in the dust as sulphate,

When the fertilizer companies began to purchase low grade material for potash, one of the first substances which attracted their attention was the crust which collects on the inside walls of the stacks of the rotary kiln and which falls down at intervals into the dust chamber, its high potash content having been pointed out by the writer in a paper read before the Cement Manufacturers and also in former editions of this book. They persuaded a number of the cement manufacturers to save this crust which

[1] See page 312.
[2] See page 315.

they purchased at prices ranging from $1.50 per unit in the early days of the war to $3.00 per unit later on. This dust averages 6 to 8 per cent (or units) of water soluble potash.

The Security Cement & Lime Company, Security, Md., were among the cement companies who sold their flue dust. Later on in 1916 they installed the Cottrell system and from that time until the close of the war collected from $800 to $1,000 worth of potash daily. Numerous other plants installed collectors but only a few of them made any money.

Water Soluble Potash

One very peculiar situation presented itself when the collector at Security was placed in operation, which has not been foreseen. At the plant of the Riverside Portland Cement Company, practically all of the potash in the dust was in the water soluble condition. At Security, it was found that only a little more than half of the total potash in the dust was water soluble and that while the dust contained from 12 to 15 per cent total potash it contained only about 6 to 7½ per cent of water soluble potash. The only explanation which could be offered to account for the difference in the state of the potash at the two plants was that at Security the cement was burned with pulverized coal and at Riverside with oil. It appears, therefore, that chemical combination takes place between the ash and the potash both of which are in a state of extreme mechanical subdivision.[1]

It was found, however, that all of the potash in the dust may be dissolved by prolonging the digestion with the hot water or by digesting under high pressure. It is also readily soluble in acid. In making mixed fertilizers with this dust it was found that a considerable portion of this potash was rendered soluble when the dust was mixed with acid phosphate.

It has, of course, been known that chlorides will increase the volatilization of potash. The plan which proved most successful was to introduce a small amount of salt with the raw material and also with the pulverized coal. By doing this the liberation

[1] Potler and Cheesman, *J. Ind. and Eng. Chem.*, Vol. X, p. 109.

of potash was materially increased and the recombination of the potash prevented due to the saturation of the ash by the soda in the salt. Huber and Reath (U. S. Pat. Nos. 1,194,344 and 1,219,-315) proposed to use calcium fluoride in place of salt. They claimed that where the potash is leached from the dust the fluoride is entirely recovered by the treaters so that only a very small quantity of this mineral is needed, the original charge passing around in a cycle as it were.

The soda as well as the potash is volatilized to some extent so that the dust will contain some water soluble soda. Usually the proportions are about 1 of soda to 3 or 4 of potash.

As practically all the potash in kiln dust can be slowly extracted with water it is highly probable that all of the potash in this material is available for plant food. In addition to the potash, this material is rich in lime so that we have in this one material two very valuable fertilizer ingredients, lime and potash.

Potash Salts from Dust

The Riverside Portland Cement Co., the Security Cement & Lime Co., the Santa Cruz Cement Co., and the Southwestern Portland Cement Co. all made potash salt of more or less purity during the last year of the war. The process at Riverside is typical and was as follows:

The dust was deposited from the treaters into cylindrical tanks filled to a depth of about 6 feet with water heated by means of live steam to a temperature of 85° C. The tanks were provided with agitators and the mass was continually stirred. After the dust was charged into the water the temperature of this latter rapidly rose to the boiling point due to the hydration of the quick lime contained in the dust. The whole operation of extracting the water soluble potash from the dust was accomplished in about fifty minutes. From the tanks the slurry was run by gravity to an Oliver filter press, its temperature being maintained at 85° C. by steam coils and the separation of the solids from the solution being affected by the filter press. The solution was stored in shallow concrete tanks which served as an evaporating pond where under the influence of the very dry climate of

Southern California, considerable evaporation took place. When the liquid attained a specific gravity of about 1.1 it was pumped to evaporating pans. As the solution became concentrated the salt dropped to the bottom. It was then raked out on to drain boards where it was allowed to remain some minutes and then deposited in a hopper where the draining continued for several hours. From this hopper it was passed through a rotary dryer and thence through a Williams mill which reduced it to the desired fineness for the market.

The loss of potash during burning in any cement plant may be proved and the quantity easily determined. To do this an average sample of the raw material should be taken before it enters the kiln and a sample of the clinker collected at the same time. It is hardly necessary to say that these samples should be representative and the kilns must be operating under normal conditions. The samples of clinker and raw material should then be analyzed to determine the percentage of potash contained in these.[1]

Since there are approximately 600 pounds of raw material required to make a barrel of cement, if we multiply the percentage of potash in the raw material by 6, we will obtain the total quantity of potash in pounds entering the kiln in the raw materials necessary to produce one barrel of clinker. There are approximately 380 pounds of clinker required per barrel of cement; hence, if we multiply the percentage of potash in the clinker by 3.8 we will obtain the quantity of potash in pounds leaving the kiln per barrel of clinker. The difference will be the amount of potash in pounds liberated and volatilized per barrel of cement.

For example, suppose the raw materials contain 0.95 per cent potash and the clinker 0.80 per cent potash then:

		Lbs.
Potash in raw material to burn 1 bbl. of clinker =	$6 \times 0.95 =$	5.70
Potash in 1 bbl. of clinker =	$3.8 \times 0.8 =$	3.04
Potash volatilized per bbl. of cement =		2.66

This is equivalent to 2.66×1.58 or 4.20 lbs. of muriate (KCl).

[1] See Chapter XVI.

The U. S. Bureau of Soils (Bulletin No. 572) found that the potash in the raw mix as fed into the kilns at different cement plants ranges from 0.20 per cent potash at the plant of the Universal Portland Cement Co., Duluth, Minn., to 1.16 per cent potash at the plant of the Three Forks Cement Co., Trident, Mont. The former plant uses a slag-limestone mix. The average loss as shown by the Bureau's figures is 1.93 pounds of potash per barrel of cement, or eliminating the plants using slag and limestone as raw materials, 2.09 pounds.

The writer made some experiments on the possibility of making Portland cement using feldspar (a mineral containing from 8 to 17 per cent potash) in place of clay and adding iron ore to supply the deficiency of iron oxide. The cement obtained from this mixture was normal in chemical composition and physical properties and from 6 to 7 pounds of potash was liberated per barrel of clinker burned.

The production of potash salt or even the potash bearing dust has been discontinued by most cement manufacturers, and if practiced at all now is in connection with dust recovery systems where the prevention of a nuisance is the object sought and not pecuniary gain from the sale of potash.

CHAPTER XIII

BURNING (CONTINUED)—FUEL AND PREPARATION OF SAME

As has been said, the principal fuels used for burning cement are pulverized coal, oil and natural gas. It will be conceded by all that the wonderful growth of the American cement industry was made possible by the rotary kiln and that the success of the latter in turn has been due largely to the use of pulverized coal. The rotary kiln is peculiarly adapted to American conditions—large output, expensive labor and cheap fuel. As originally introduced in the cement industry in the early nineties, it was heated by fuel oil and unquestionably its early development was hastened by the use of this fuel because of the simplicity of its application and the ease with which an oil flame can be regulated. About 1895, however, the price of oil having risen appreciably, cement manufacturers sought a cheaper fuel. Experiments were made with pulverized coal which proved so successful that in a few years this fuel was adopted by all cement manufacturers, except those located in natural gas belts or where fuel oil was cheaper.

Pulverized coal has no advantages over fuel oil or natural gas aside from the fact that it is cheaper in most localities. Unquestionably natural gas is the most perfect fuel because air itself is a gas and two gases can be thoroughly mixed so that each particle of one comes in contact with the other. Liquid fuels do not burn well except from a wick or when atomized or sprayed. In the latter condition, a mist is formed which approaches a gas in the mobility of its particles. The composition of both natural gas and oil is such that no contamination of the cement results as is the case with coal. Oil, therefore, was at one time very generally used for burning white Portland cement in order that no iron oxide might be introduced into the latter. The only element in oil and natural gas which might possibly prove objectionable is the sulphur. Oil sometimes contains considerable of this element, but this does not enter the cement at the high temperatures of the rotary kiln. The choice of fuel for the kiln, therefore, is purely

a matter of cost. Fig. 96 shows diagrammatically the relative cost of various fuels and by reference to this it will be seen which fuel is most economical. In comparing various fuels the cost of handling and use must be considered and in this table due consideration has been given to this.

To use the chart in comparing two fuels; if oil or natural gas is used, refer to the bottom of the chart and run up the nearest vertical line until the curve representing this fuel is reached, then

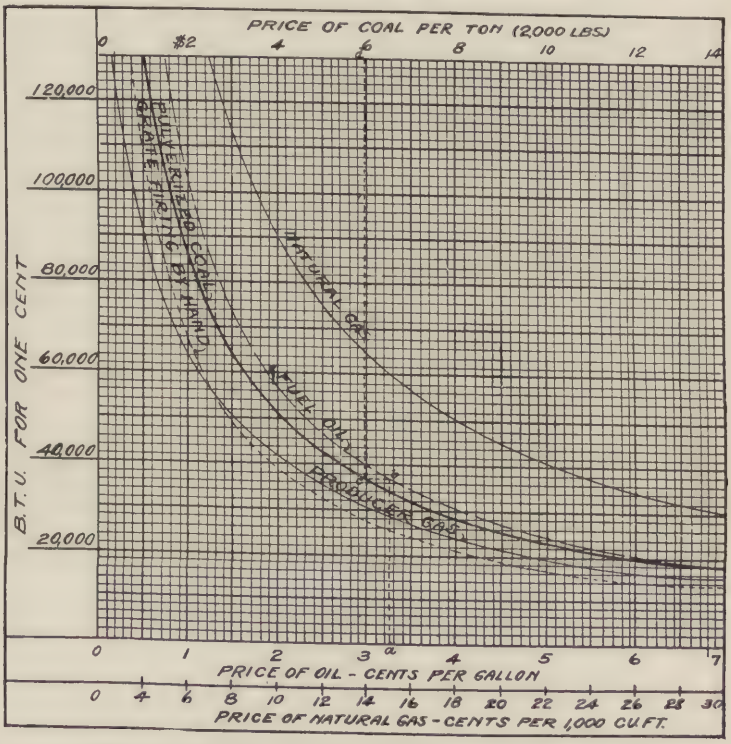


Fig. 96.—Relation between cost of fuels, efficiency, and cost of preparation being considered.

Note: Natural gas, efficiency, 90 per cent; cost of preparation, $0.00. Fuel oil, efficiency, 90 per cent; cost of preparation, ¼ cent per gallon. Grate firing, efficiency, 65 per cent; labor, 75 cents per ton. Producer gas, efficiency, 80 per cent; cost of preparation, $1.50 per ton. Pulverized coal, efficiency, 90 per cent; cost of preparation, $1 per ton.

along the nearest horizontal line until the curve representing pulverized coal is reached, and then up the nearest vertical line to the upper margin where the corresponding price of coal will be found. If it is desired to start with pulverized coal, reverse the process and start at the upper margin, etc. *For example,* to find what price coal used in the powdered condition is equivalent to oil at three and one-half cents per gallon, we find this to be $6.00 per ton. The dotted line *abcd* indicates the course to be followed to reach this conclusion.

Cost of Pulverizing Coal

With efficient apparatus the cost of preparing pulverized coal is about that shown in Table XXVIII.

TABLE XXVIII.—Cost of Pulverizing Coal, Central Plant System

Item of expense	Quantity to be pulverized in 8 hrs. in tons			
	50	100	150	250
Dryer fuel	$.087	$.087	$.087	$.087
Labor	.300	.200	.160	.120
Repairs, supplies, etc.	0.73	.073	.073	.073
Power	.150	.150	.150	.150
Milling cost per ton	.600	.510	.470	.430
Interest and depreciation	.500	.300	.250	.170
Total cost per ton	$1.100	$0.810	$0.720	$0.600

*The above costs are based on dryer coal at $6 per ton and 8 per cent moisture in undried coal, labor at 50 cents per hour and power at one cent per kw-hr. Interest and depreciation are figured at 15 per cent of cost of plant and 300 days' operation, 8 hours per day.

Composition of Coal for Cement Burning

Formerly it was believed that the only coals suitable for burning in the pulverized condition were those high in volatile matter such as bituminous coal and lignite. This supposition was based on the fact that such coals ignite more readily than do the low volatile coals. This belief was no doubt also due to some extent to the fact that coals rich in volatile matter (the so-called soft coals) are much more easily pulverized than are the anthracite coals, the latter being difficult to pulverize. It also happens that up until the time of the World War, slack coal or "screenings" could be obtained much more cheaply than could run-of-mine and lump coal. This slack is usually high in volatile matter,

and possibly for this reason was considered most desirable. As a matter of fact, the employment of high volatile coal was influenced largely by the low price at which this fuel could be obtained and the ease with which it could be pulverized.

It is quite probable that the prices being equal, high volatile coal is to be preferred because the rapidity with which it ignites would seem to make fine grinding less necessary; its soft structure also makes pulverizing comparatively easy. The temperature of the flame obtained from powdered coal, however, is so high, ranging as it does from 2,500 to 4,000° F., that practically all grades of coal can be burned under suitable conditions. Given a number of coals to select from the question would be one of economy—that is to say, the cost of the coal delivered, the expense of its preparation and its thermal value, rather than its chemical composition.

The coal now most generally employed for burning is gas slack and should fill the specifications below:

	Per cent
Volatile and combustible matter	30-45
Fixed carbon	49-60
Ash, as low as can be obtained cheaply and not over	25

In the Lehigh district good gas coal can be obtained with less than 12 per cent ash. In other sections, however, poorer coal has often to be bought. The ash, when under the limit specified, of course merely takes away from the fuel value of the coal. Above this limit it is hard to burn satisfactorily. Sulphur has no effect on the burning, except in large quantities. Iron pyrites are hard, and consequently may not pulverize. When coal containing much of this is used the pyrites may remain in coarse crystals after grinding, which are not blown in the kiln and burned, but fall from the nozzle of the burner among the clinkers and remaining unoxidized, are ground with the clinker, causing the resulting cement to develop brown stains. Practically none of the sulphur of the coal enters the cement, except as above.

TABLE XXIX.—Analyses of Coals Used for Burning Cement

From	Moisture Per cent	Volatile combustible matter Per cent	Fixed carbon Per cent	Ash Per cent
Wellston, Ohio	2.94	41.96	42.82	12.27
Connellsville, Pa.	1.38	35.04	56.03	6.27
Fairmont, W. Va.	2.15	34.20	57.49	6.16
Alabama	7.50	30.70	53.80	8.00
Hocking Valley	0.82	33.76	61.57	3.85
Illinois	6.59	34.97	48.85	8.00
Poor quality Penn'a.	2.10	29.63	51.28	16.99
Poor quality Penn'a.	2.32	27.08	47.34	23.26

Preparation of the Pulverized Coal

As to the preparation of the powdered coal itself, this will depend to some extent on the system which is used for burning. In general, two systems are employed—in one of which the coal is pulverized in a central plant and conveyed either mechanically or with air to the point of use ("Central Station System"). This system is employed by practically all cement manufacturers using coal for burning. In the other system, the pulverizer is located adjacent to the furnace and the coal is blown into the latter by a current of air which passes through the pulverizer. This system known as the "Unit System" is employed at only a few mills.

Where the coal is pulverized in a central plant, it is conveyed into bins at the kilns and is fed from these bins as desired and blown into the kilns with air. In this system, the central plant usually consists of some form of coal crusher in order that run-of-mine and large size coal may be handled, a dryer and one or more pulverizers. The details of this equipment are given below.

Coal Crushers

In the older plants, the coal was usually crushed between rolls or in a small "pot-crusher." This latter resembles most an ordinary hand coffee mill in which the grinding is done between corrugated surfaces. It is suitable for small installations only and is generally considered inferior to the special forms of coal crusher now on the market. Where a pair of rolls is used these are usually provided with heavy spikes or teeth. These two-roll or "Cornish" rolls as they are sometimes called are still much used in coal breakers where crushing of the coal finer than two and

one-half inch lumps is not necessary, but are not adapted to finer work.

As I have said, both of these forms of crusher are now largely superseded by special coal crushers of the "Single-Roll" type. These latter (Fig. 97) consist of a cast-iron frame on which is mounted a crushing roll which revolves against a concave breaker plate. The roll is usually provided with teeth. The breaker plate is hinged at its upper end and is provided with arrangements for adjusting the clearance between the roll and the plate. The size of the product is regulated by this opening. The roll is

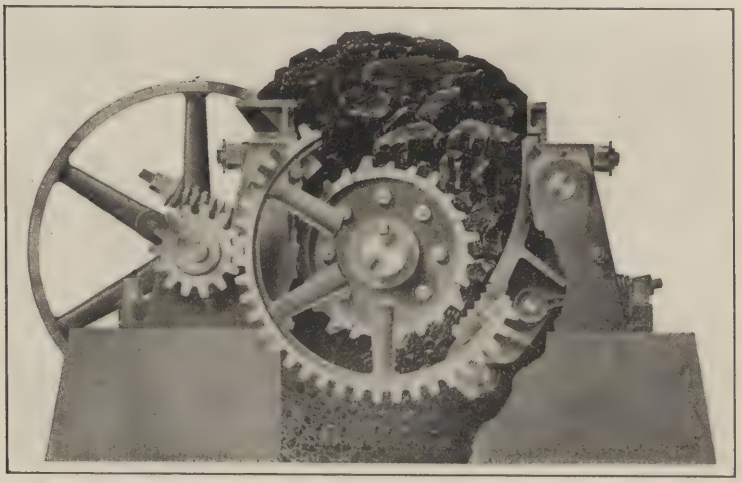


Fig. 97.—Single roll coal crusher—Pennsylvania Crusher Co.

usually driven by means of a countershaft mounted on the frame through a pair of gears. The coal is broken between the roll and the plate. These machines are adapted to handle large lumps of coal and very wet material and will reduce the product to one inch and under. The fineness to which the coal should be crushed will depend on the size and type of pulverizer used, but one inch lumps are sufficiently small for any pulverizer used in a cement mill.

The following are the usual sizes and capacities of single roll crushers when taking Ohio and Illinois coal and reducing to one inch lumps and under. When operating on Pocahontas and other

soft bituminous coal the capacity is about double that given in the table. The capacity is also increased if a coarser product is desired.

TABLE XXX.—CAPACITY OF SINGLE-ROLL COAL CRUSHERS

Size crusher Opening—inches	Approx. H. P.	Capacity in tons per hour	
		1 In. material	1½ In. material
18 x 18	15	20	30
24 x 24	30	50	70
30 x 30	40	75	100
36 x 36	60	115	150

Drying the Coal

In order to get the greatest efficiency out of the pulverizing machinery, it is necessary to dry the coal so that it does not contain more than 1 per cent moisture. Still better results will be obtained if the moisture is reduced to about one-half per cent.

For cement burning, where the stack gases leave the furnace at a high temperature, there is no economy in grinding coal without drying, and often there is some objection in such practice. For example, if the gases leave the furnace at a temperature of 2,500° F., every pound of steam carries out 2,600 B. t. u., while at 400° F. the average temperature of dryer waste gases, the steam only carries off 1,300 B. t. u., or about half as much. It is only fair to say, however, that with coal containing 10 per cent moisture, this would only represent a loss of about 1 per cent of the heating value of the coal; so that this objection is theoretical rather than practical.

The drying temperature should not be allowed to exceed 212° F., by any considerable degree as otherwise some of the volatile matter of the coal will be lost. If kept around this temperature, there is no danger of driving it off.

Several forms of dryer are now used for drying coal. The simplest of these is a properly designed direct-heat dryer. Other forms in common use are the Ruggles-Coles dryer and the Matcham or Fuller-Lehigh dryer.

Fuller-Lehigh Dryer

The Matcham dryer was developed in the Lehigh District of Pennsylvania and is used quite extensively in the cement industry. It was the design of the late Mr. Charles A. Matcham, of Allentown, Pa. This dryer with some modifications and improvements is now on the market under the name of the Fuller-Lehigh Dryer.[1]

[1] Fuller-Lehigh Company, Fullerton, Pa.

In this latest form it consists of an inclined cylinder mounted on steel tires which revolve on rollers. The cylinder is turned by means of a girt-gear and pinion at an approximate speed of one to four revolutions a minute. The inclination of the cylinder is approximately five-eighths of an inch to the foot and it revolves partly in the brick housing which contains the furnace. The hot gases pass up around the cylinder and thence through a short flue to the discharge hood and from this up through the cylinder. Draft is provided either by meàns of a stack or an exhauster fan. The latter is to be preferred. (See Fig. 98).

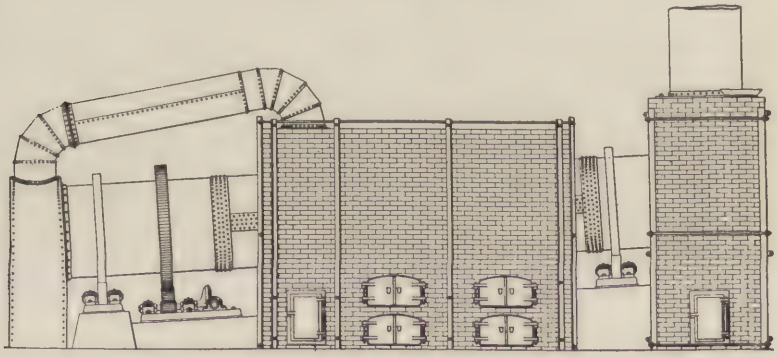


Fig. 98.—Matcham coal dryer.

The coal is fed in at the upper end of the cylinder and owing to the inclination of the shell, the material is gradually moved forward as the cylinder revolves until finally it reaches the lower end of the cylinder where it drops out into a hopper and from this latter it is usually spouted to the boot of an elevator. Z-bars or other forms of lifters are bolted to the inside of the shell and as

the cylinder revolves these lift the coal and drop it in a steady cascade through the hot gases from the combustion chamber, which are passing through the cylinder. This exposes a large surface of coal to the drying action of the gases and tends toward efficient drying.

This dryer is made in various sizes. These are given in Table XXXI together with the power required to operate and the capacity based on coal having less than 10 per cent extraneous moisture, as stated by the manufacturer.

TABLE XXXI.—CAPACITIES OF FULLER-LEHIGH DRYERS

Size		Capacity per hour Tons	Power to operate H. P.
Diam. Ft.. in.	Length Ft.		
3-0	20	2	5
3-0	30	4	8
3-6	30	6	10
4-6	30	8	12
4-6	42	10	15
5-6	42	14	17
6-0	42	20	20
6-6	42	25	24

Ruggles-Coles Dryer[1]

The Ruggles-Coles (Class A) Dryer consists of two concentric cylinders which are fastened together and revolve on steel tires supported by rollers. The dryer is revolved as in the case of the Matcham Dryer by means of a girt-gear and pinion. The inner cylinder extends beyond the outer one at the head end and is connected with a brick furnace by a flue lined with fire brick. The coal is fed into the head end of the dryer between the two cylinders and is caught up by flights on the inside of the larger shell and dropped on the hot inner shell. As the machine continues to revolve, the coal in turn drops from the inner shell to the bottom of the larger one, is carried up by the flights and again dropped on the hot inner shell, etc., and gradually works its way through the cylinder due to the inclination of the latter. (See Fig. 99).

The hot products of combustion pass from the furnace down through the inner cylinder and then back between the shells.

[1] The Hardinge Co., New York, N. Y.

Draft is induced through the cylinders by means of an exhaust fan. The drying is effected by means of the hot inner shell and the current of hot gases to which the material is subjected. Fully

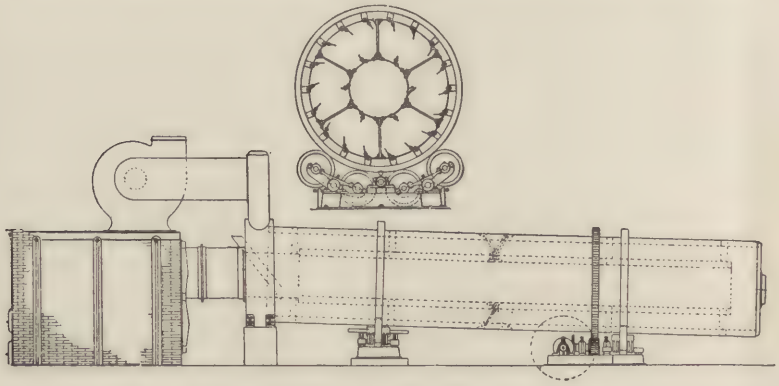


Fig. 99.—Ruggles-Coles dryer.

dried coal is discharged through the center of the rear end by means of a special arrangement of lifting plates.

This dryer also is made in a number of sizes which are indicated below.

TABLE XXXII.—Size, Capacity, Etc., Ruggles-Coles Dryers

No.	Diameter outer cylinder In	Length outer cylinder Ft.	Capacity in tons per hr.	Power to operate
A-1	36	16	2	6
A-2	48	20	4	10
A-4	54	26	5½	12
A-8	60	30	8½	16
A-10	70	35	13½	20
A-12	80	45	18½	33
A-14	90	55	24	45

Both the Fuller-Lehigh and Ruggles-Coles Dryers are what are known as "Indirect Fired Dryers"—that is, the gases from the furnace do not come directly in contact with the material to be dried but are first allowed to cool somewhat so that when they come in contact with the coal being dried, there is no danger of the latter being ignited or even suffering the loss of any of its volatile content.

Direct Fired Coal Dryer

By so placing the combustion chamber that there is no possibility of any flame coming in direct contact with the coal being dried, it is possible to use direct-fired dryers for drying coal and many of these are now so used. In order to accomplish this result, it is only necessary to set the grate at a sufficient distance from the end of the cylinder to have the gases of combustion cool below the point at which the coal ignites. This is accomplished by placing a brick chamber between the fire box and the cylinder. The cooling of the gases is also facilitated by leaving openings in the chamber between the grate and the end of the cylinder so that air can be mixed with the products of combustion and further cool these.

It is desirable in the case of these dryers to install a pyrometer where the gases enter the cylinder in order that the temperatures may be controlled. This pyrometer should be attached to an automatic governor by means of which air is added to the furnace gases to cool these as needed. While the entrance of the air cools the combustion gases, it does not necessarily detract any from the efficiency of the dryer, because hot air itself is an excellent medium for drying. Everyone is familiar with the rapidity with which a substance may be dried if it is placed in a current of warm air. This is due to the capacity of air for taking up moisture and this capacity to take up moisture increases with the temperature of the air. For instance, 100 cubic feet of air at 60° F. will absorb approximately 0.082 pound of water. If we heat the temperature of this air, however, to 100° F. it will increase to 108 cubic feet and will absorb 0.305 pound or about four times as much. This difference becomes much more marked when we heat the air to higher temperatures. This action increases very markedly the efficiency of both the direct and indirect types of dryer. A fan is desirable to furnish draft in the case of any dryer because of the larger volume of air which may be employed thereby.

The capacity of a direct-heat dryer is greater than that of an indirect dryer of the same size. Table XXXIII gives the aver-

age figures for direct-fired dryers of various sizes when drying coal containing 10 per cent moisture.

TABLE XXXIII.—Capacity and Size of Direct Fired Coal Dryers

Size		Capacity in tons per hour	H. P. to operate with stack draft
Diam. Ft., in.	Length Ft.		
4-0	40	7-8	7½
4-6	45	10-12	10
5-0	50	12-14	15
6-0	60	17-20	20

In the cement industry it is usual to discharge the gases from the coal dryer directly into the air by means of a stack or fan. The more modern practice, however, is to discharge the gases into a cyclone collector and from this into the air. The cyclone collector is, of course, designed to catch the fine particles of coal which are carried out by the gases and so reduce the dust loss from the dryer.

It is possible to fire any of the three types of dryer mentioned by means of pulverized coal. The powdered coal must be burned in a Dutch oven of appropriate design and care, of course, must be exercised that the flame does not extend so far beyond the nozzle of the burner that it will reach and ignite the coal being dried.

The dryers are usually fed from an overhead bin by means of some mechanical device such as a reciprocating feeder or a revolving table. The former is the more usual method. The feed is attached to the driving mechanism of the dryer so that when the dryer ceases to revolve the feed stops.

Pulverizing the Coal

Four types of pulverizers are now in general use for pulverizing coal, while several more are in use at a few plants only. In the early days of the cement industry, the Griffin Mill was quite generally used for pulverizing coal, but while still used to some extent in this industry, it is not, so far as we know, being installed in any new plants. The types of pulverizer now most commonly used are the Fuller-Lehigh and Raymond Mills. A

few plants employ tube-mills and one or two, Bonnot Mills. Fuller, Raymond, Bonnot and Griffin Mills are self-sufficient units, but the tube mill requires that the coal shall be prepared for it by some other grinder which will reduce the coal to approximately 10- to 16-mesh material. All these mills are described in Chapter X.

The tube mill is not so well adapted to pulverizing coal as the first mills referred to. The principal objection raised to the high speed mills has always been one of repairs, as it is generally conceded that they are so far as power goes, more economical grinders than the tube mill. Coal, however, is soft and easily ground if properly dried and the repairs in the case of ordinary bituminous coal free from pyrite are low, so that the objection raised to the high speed mill for grinding clinker will not hold here. In addition to the advantage of being a self-sufficient unit, the high speed mills require less floor space and do away with the extra elevator and bin necessary for the two-stage reduction.

The tube mill requires that the coal fed to it shall be ground so that all of it will pass a 10- to 16-mesh screen. This latter operation is usually conducted in a ball mill, a kominuter, or more frequently in some form of hammer or cage mill such as the Pennsylvania, Williams or Jeffrey hammer mills or the Steadman Cage Disintegrator. The good points of the tube mill are its simplicity and the fact that repairs were exceptionally low. Its bad features are high power consumption per ton of output, large floor area required by the installation and the disadvantage of

TABLE XXXIV.—Capacities of Tube Mills Grinding Coal

Size		Mill charged with pebbles			Mill charged with steel balls and pebbles			
Diam. Ft., in.	Length Ft.	Weight of charge of pebbles—lbs.	*Output in tons per hour	H. P.**	Weight of steel balls	Weight of pebbles	*Output in tons per hour	H. P.**
5	22	20,000	5	80	9,000	15,000	8	100
5-6	22	24,000	6½	100	11,000	18,000	10	120
6	22	29,000	8	125	13,000	22,000	13	150

*Mill to receive a feed all of which will pass a 16-mesh screen.

**About 150 per cent of this power is required for starting. This does not include power required to prepare feed for the tube mill which will add about 35 per cent to above figures.

the two-stage process, necessitating as it does an extra mill, bin and elevator.

The output and horsepower required to drive tube mills, when grinding bituminous coal of average hardness to a fineness of 95 per cent passing the 100-mesh sieve is given in Table XXXIV.

General Coal Plant Arrangement

Run-of-mine and even screened coal often contains scrap iron such as parts of mine machinery and cars, bolts, nuts, etc. These are apt if they enter the pulverizer to cause break-downs or at least excessive wear to the latter. It is now, therefore, general practice to protect the pulverizer by the employment of a magnetic separator at some point before this. The form of separator generally used consists of a magnetic head pulley over which the conveyor belt passes. This serves to divert the iron from the coal discharge and so free the latter from the former.

It is now quite general to include automatic recording scales at some convenient point before the dryer. These are usually placed at either the discharge of the elevator which carries the coal up into the dryer feed bin or else between the bin and the dryer. The coal as it drops from the dryer is usually led by a hopper and spout into the boot of a bucket elevator and carried up into a bin which feeds the pulverizers.

In the early days of the cement industry several bad fires and explosions occurred in connection with the pulverizing of coal. As the result of this the danger of an explosion was at one time often raised as an objection to the use of powdered coal. This latter danger, however, was always very largely exaggerated and it has now been many years since an explosion occurred in the coal pulverizing department of a cement plant.

Powdered coal *suspended in air* is a very explosive substance and indeed the energy of a pound of coal in this condition is greater than that of a pound of gunpowder. At the same time, however, powdered coal *in a mass*, that is, when it is in a pile or a bin, burns very slowly and with absolutely no explosive effects.

The idea, therefore, in preventing coal mill explosions is not to allow the coal dust to be stirred up and mixed with air.

The department of the plant in which the coal is ground should always be well ventilated so that no gas can accumulate. This can be accomplished by the use of a monitor running the full length of the roof and having louvers so that any gases which may be generated from the coal will rise to the roof and so escape In place of the monitor, any of the accepted forms of roof ventilator can be used. Reinforced concrete offers a splendid material for the construction of fuel-mill buildings as the walls are straight and there are no projections to catch dust.

In order that any fires which start in the coal pulverizing department may not be communicated to other parts of the mill, this building should be fireproof and located with at least an alley between it and the other parts of the mill. Stairways, bins, platforms, conveyor troughs, elevator casings, etc., should be made of sheet steel. Platforms and steps should be constructed of perforated sheet steel, or better still Irving's Subway Grating, or some similar form of bar grating may be used to advantage, as less dust collects on them in consequence.

The electrical wiring of the mill should be carefully installed and the lights placed to best advantage. The latter should be of the incandescent type. Arc lights are not permissible. Most fires in coal mills result from attempts being made to repair elevators and mills by the light of the ordinary workman's torch. The hammering shakes the dust from its lodging place and the naked flame ignites the mixture of dust and air. No naked lights should be allowed at any time in the coal pulverizing building and warnings against the uses of torches, etc., should be displayed prominently here and large signs to the same effect should be placed upon the doors. This rule should be rigidly enforced with the penalty for breaking it of dismissal.

Conveying the Coal

With all of the types of pulverizer which have been described, the powdered coal is conveyed from these to a large bin or num-

erous small ones located adjacent to the kilns. Until very recently, the practice in the cement industry has been to convey the coal to the point of use by means of a screw conveyor and bucket elevator. This could be easily done because with the exception of a very few plants where the raw material dryers were also heated with pulverized coal, this latter had to be conveyed only to the kilns. This permitted the fuel pulverizing building to be located adjacent to the kiln building and one straight screw conveyor carried the powdered coal to the kiln bins. In some instances the coal mill and kiln building adjoined each other. It was generally considered better practice, however, to have at least an alleyway between the kiln building and the coal mill. At a few plants, screw conveyors of several hundred feet were required to carry the coal to the kiln building but at most plants a conveyor half this length was sufficient.

The more recent installations for handling coal in the cement industry employ the Fuller-Kinyon system. A "blow-tank" system is often employed for conveying powdered coal in metallurgical plants but this latter method has never found use in the cement industry.

Fuller-Kinyon Pump

The Fuller-Kinyon system consists of four elements:

1. A power-driven pump, the function of which is to start the mass in motion.
2. A source of compressed air supply.
3. A pipe line through which the material flows.
4. Diverting valves which permit the flow of material to be discharged through any one of a number of branch lines leading into the kiln service bins.

The pump (Fig. 100) embodies a specially designed worm or screw revolving in a closed chamber or working barrel. The screw is mounted on an extension shaft which passes through end packing boxes in the casing and is supported on outboard bearings. This arrangement prevents contact between the bearing metal and the pulverized material. The screw is usually

driven by a direct-connected motor. A separate motor-driven air compressor is provided to furnish the necessary air for aerating the coal. However, where an air compressor is already installed in the plant, this unit is depended upon for the air supply.

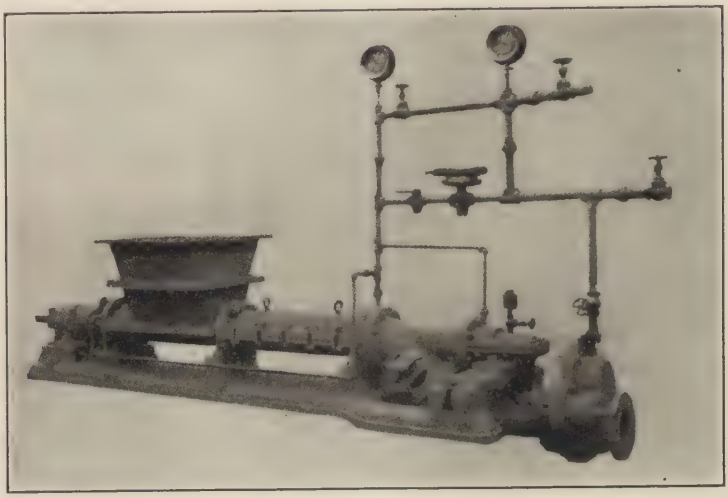


Fig. 100.—Fuller-Kinyon coal pump.

Pulverized coal is fed from the storage bins or from the Fuller mills direct into the pump hopper by gravity and is carried by the screw to the discharge end. The design of the worm is such that the material is compressed as it moves forward so that at the end of the worm it is dense enough to act as a seal or check against the compressed air and prevent the latter from blowing back into the feed bin.

At the discharge end of the screw, the mass is aerated by a small amount of compressed air at moderate pressure. The pressure and amount of air are regulated and depend upon the distance, height, etc., to which the material must be conveyed. This aeration changes the nature of the material from a compact mass to a semi-fluid, in which state it is carried to its destination. The amount of air used is so small that no cyclone separator or dust collector is required at the point of delivery. An extra air line,

by-passing the pump, is supplied so that the pipe line may be cleared of material whenever the pump has been stopped.

The pump, consisting of a 6-inch worm, is capable of handling upward of 50 tons of pulverized coal per hour, and easily handles material a distance of over 1,500 feet. The power is approximately the same as would be required for screw conveyors and elevators doing the same work. The air pressure required varies from about 15 pounds per square inch for short distances to about 45 pounds for longer distances. The air volume varies from 6 to 8 cubic inches free air per cubic foot of pulverized coal handled.

Distribution Line

The conveying line is usually built of ordinary black or galvanized iron pipe properly jointed to eliminate recesses in which particles might lodge. The diameter depends upon the quantity of coal to be transported, but ordinarily varies from 3 inches to 5 inches. The pipe line may be carried in the most convenient manner such as on overhead supports, laid underground, or placed on the surface to follow the natural slope of the land. Bends, elevations and depressions do not decrease the satisfactory operation of this system, although no doubt as with liquids they increase the frictional resistance to the flow of the coal and hence increase the power or air required.

Distributing valves are placed in the main line at points where the main flow is to be diverted to one or more branch lines. In the Fuller-Kinyon system, these are of the disc, multiple discharge type and are electro-pneumatically controlled from a convenient point. Their action is positive, preventing the flow past the ports which are in closed circuit and at the same time allow unobstructed passage through the open main.

The individual kiln bins may be equipped with indicators showing the condition of the contents of the bin. In the Fuller-Kinyon system, there are high and low point indicators, which automatically and instantly reflect the condition of the bins on the switchboard located at any convenient point in the coal prep-

aration plant. Thus the operator under this system has constant intimate knowledge of the fuel supply in all the bins throughout the plant, and by means of the electro-pneumatic valves he can instantly direct the flow of material from the main line to any individual point without leaving the coal house.

Equipment Employed for Heating the Kiln with Powdered Coal

The apparatus originally developed in the cement industry is shown in Fig. 101. This arrangement is more or less typical of

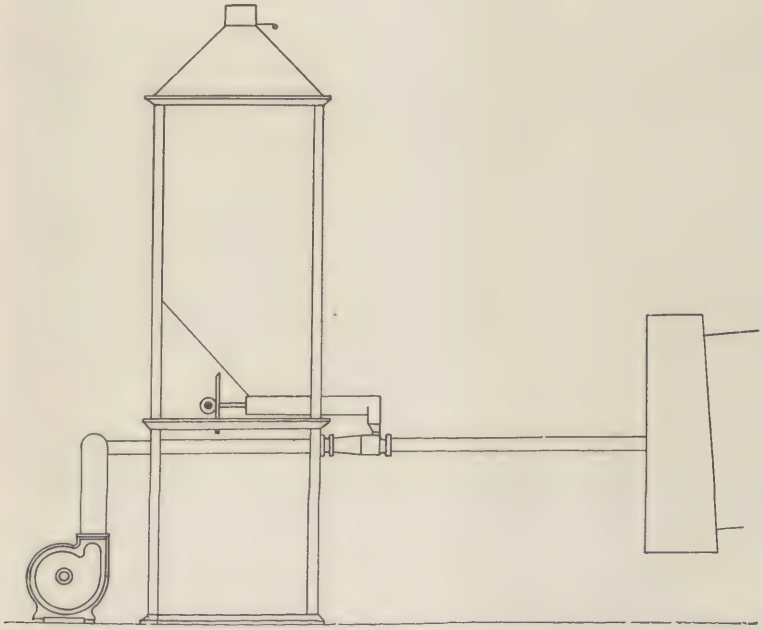


Fig. 101.—Method of burning powdered coal. (B. F. Sturtevant Co.)

modern powdered coal installations also. It consists of a bin in which the pulverized coal is stored, a worm feeder from which it is delivered into an injector through which air is forced by a pressure blower. The injector may be of cast iron, but it was quite common in the cement industry to have them made of gal-

vanized iron by a local tinsmith. The blast pipe leading to the kiln is often also of galvanized iron, in which event it terminates in a nozzle of wrought iron which projects for a foot or more through the hood into the kiln. Lap-welded steel or wrought iron pipe, however, makes a much neater and more permanent job than galvanized iron. The worm is operated by means of some form of variable speed control. (See also Fig. 104).

The feed bin does not differ materially from other bins except that it should have a hopper bottom and the sides of the latter should be steep. It is always best to have one side perpendicular as shown in the drawing and still better results will be obtained if three sides are perpendicular, as this gives less hold to the toe of the arch. The bin should, of course, be dust-proof. It should be made of steel plate and supported on a light frame of structural steel made without cross-pieces. Steel tanks are sometimes used but are less desirable than the hoppered bottomed square bins. Round bins with cone-shaped hoppers are also used but the square bins of the type described are to be preferred to these also. As pulverized coal is perfectly dry, no corrosion will occur in these bins from the sulphur in the coal, as happens when steel bins and bunkers are employed in connection with stokers.

Air for Carrying Coal

It will be recalled that theoretically approximately 10 pounds of air are required to burn a pound of coal. This weight of air occupies under ordinary temperature and pressure a volume of 125 cubic feet, while one pound of coal neglecting voids has a volume of less than 0.012 of a cubic foot. It will be seen, therefore, that if this volume of coal is blown into a furnace with at least 25 per cent of the air necessary for combustion (or 34 cubic feet) that the volumes of coal and air will bear respectively the relation of 1 to 2,833.

There is, of course, no objection to increasing the air to the full amount required by theory, and indeed this is often done, when the volumes will be as 1 to 11,332. It will be seen, therefore, that provided the coal is dry and the particles are not clotted

together by moisture, etc., there is ample opportunity for the coal particles to be surrounded with sufficient air to at least cause their ignition. In cement burning, instantaneous combustion is not only unnecessary but, in fact, is not desired, the only requisite for economy and the desired effect being that the particle of fuel shall be completely consumed in the forepart of the kiln.

In the early days of powdered coal, it was the practice with high pressure air (60 pounds or more) to employ about 10 per cent and with low pressure air (6 ounces or more) as little as 25 per cent of the air necessary for complete combustion. Now, however, it is becoming more and more the practice to mix with the coal in the burner a comparatively large percentage of the air necessary for combustion. Manifestly as we approach this condition more rapid combustion will occur.

In some of the earlier installations in the cement industry compressed air was used, while at a few installations a steam jet was employed. The general practice now, however, is to use an ordinary centrifugal fan or pressure blower and operate this under a pressure of from 4 to 10 ounces, which gives sufficient velocity to the air in the blast pipe to carry the coal into the furnace. These fans if properly designed and run at the speed required for this pressure give a regular and constant supply of air under uniform pressure. They are simple in construction and easily kept in repair. They consequently meet all requirements as to air supply.

Worm Feeder for Coal

The problem of supplying a regular stream of coal to the kiln, however, is by no means so simple. Practically all equipment now employed makes use of a worm or helical conveyor feeder and the amount of coal delivered is regulated by the size and speed of the screw or worm. There are objections to this form of feeder but no better device has been offered.

The amount of coal which will be fed out of a bin by a given worm revolving at a given speed under uniform conditions is definite and fixed. Unfortunately, however, these worm feeders do not work under constant conditions. The chief variable in-

fluencing the rate of feed is the quantity of coal in the bin, so that unless the coal is of the same depth in the bin at all times, the quantity of coal delivered by the worm at a given speed is apt to vary.

In practice, however, this feature is not so serious as it sounds because as the quantity of coal in the bin increases or decreases, the attendant has merely to vary the speed of the worm at intervals in order to keep the coal supply constant. The real trouble is to provide against sudden rushes of coal or a marked diminution of the quantity delivered.

Both troubles usually result from the "arching" over of the coal in the hopper part of the bin so that the coal does not flow regularly into the burner. The sudden breaking of the arch due to the weight of the coal above it, or, as often happens, the effort of the kiln attendant to break the arch by hammering on the sides of the bin, will cause a sudden rush of coal into the feeder and consequently into the kiln. This difficulty can be eliminated to some extent by proper construction of the feed bins and design of the feeder.

The worm feed is usually bolted directly to the bottom of the bin. Steel sliding plates or gates are placed between the bin and the feeder so that the coal can be entirely cut off from the latter. This allows repairs, etc., to be made to the worm without emptying the bin. The worm consists of a helical screw which revolves in a tubular housing. This screw is made of either thin steel plate or cast iron. If the former, it is usually made with flights half the pitch of the standard screw conveyor, as this gives a more regular feed and also a greater obstruction to the flow of the coal, which under certain conditions will flow around the shaft of the screw just as would a liquid. It will be noted that the worm and tube extend beyond the bottom of the bin. This is done in order to prevent the coal from flushing or flooding the burner. The tubular housing fits close to the worm for the same reason.

TABLE XXXV.—Capacity of Worm Coal Feeders Made from Standard Helicoid Conveyors. Weight of Pulverized Coal Taken as 40 Pounds to Cubic Foot.

Diam. of conveyor In.	Pitch of flights In.	Diam. of shaft In.	Thickness of flights In.	Pounds of coal per revolution Lbs.	Pounds of coal per hour at 50 r. p. m. Lbs.
3	3¼	1 15/16	0.1406	0.30	900
4	4½	1 15/16	0.1875	0.96	2,880
5	6	2 7/16	0.250	1.99	5,970
6	6½	2 7/16	0.250	3.41	10,230

The worm revolves in a casing which is usually made in several parts and according to the ideas of the maker. The writer makes the hopper part below the bin of plate metal and the tubular part extending beyond the bin of steel or cast iron flanged tubing. The chief points to be taken care of in the design of the casing are: (1) To have the tube fit the worm snugly, but at the same time the two should not actually rub: (2) To so arrange the parts that the worm can be drawn out easily for repairs to the flights, etc.: (3) To give a rigid support for the end bearing so that the shaft will be kept properly centered, and (4) To make all connections dust-proof.

The amount of coal fed out of the bin by the worm will depend on the size of the worm and of the pipe on which it is mounted, the pitch of its flights and the speed at which it revolves. As I have said, helicoid conveyors used for this purpose are often made one-half of the standard pitch and the sizes generally employed range from 3 to 6 inches conveyors. The capacity of such conveyors is given in Table XXXV. If the pitch is half the standard figures, the feeder will deliver only one-half the coal shown in this table, etc. Liberal allowance should be made from these figures in actual work.

Equipment for Reducing and Varying Feed

The shaft of the worm is usually keyed to the larger one of a pair of bevel gears and the worm is so driven. Another good arrangement is the friction disc and wheel described below. Sometime a worm gear is used and occasionally a gear and pinion.

The simplest and also the crudest method of varying the speed of the worm is by means of a pair of stepped pulleys connected by a belt such as is employed for altering the speed of machine tools, etc. The objection to such a method is that the fuel control is by steps and intermediate points between those given by the various steps are not possible; whereas kilns are often susceptible to very slight changes of fuel and one step on the pulley might give too hot a kiln and the next below, one which is too cold. The step pulleys are not now used to any extent and have been superseded by some of the patented forms of speed control such as the Reeves, the Mosser or that made by Moore & White. Another form of speed control which gives good satisfaction is that of the disc and friction pulley.

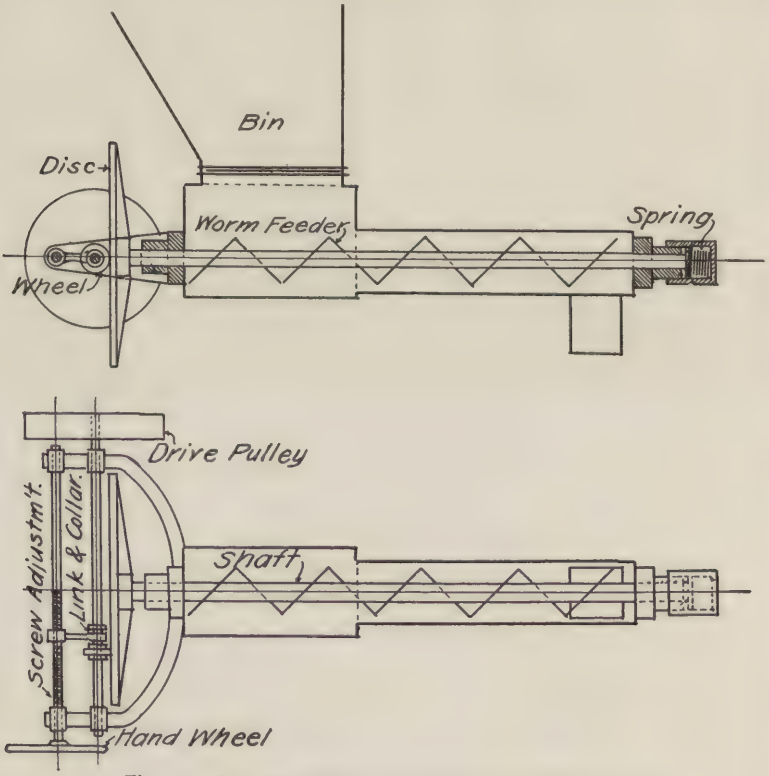


Fig. 102.—Disc and wheel worm feeder for pulverized coal.

This latter is more or less of a "homemade" affair and will be described first. It is shown in detail in Fig. 102. It consists of a friction disc which is revolved by means of a friction pulley. The disc is keyed to the worm shaft and the pulley to a countershaft driven at constant speed. The surface of the pulley is often covered with rawhide to give greater friction. This pulley is arranged so as to slide back and forth along the shaft, being moved by a screw rotated by a hand or chain wheel, which screw in turn moves a nut connected by a link to a collar on the friction wheel. Manifestly as the wheel is brought nearer to the center of the disc, the latter revolves more rapidly, etc. The pressure between the wheel and disc is kept constant by means of a spring which acts on the worm shaft.

The Reeves, the Mosser and the Moore & White speed controls are all on the market and may be obtained from the makers. When the coal feed is driven from a line shaft, they may be employed to advantage although the friction disc and wheel is simpler and in the writer's opinion is more satisfactory as the belts of the speed controls give trouble.

When motor drives can be employed nothing will answer better, however, than to employ a variable speed motor. When these latter are used the plan is to drive the shaft of the feeder by means of either a worm and gear or else to employ some form of spur-gear or worm-gear speed reducer between the motor and the shaft. It is needless to say that gears encased and running in oil are to be preferred to those without casings. A neat arrangement consists of a variable speed motor connected to the feed screw by means of a reliable worm-gear reducer.

The horsepower required to operate the feed is merely nominal. The small sizes can be driven by a 1 or 2 horsepower motor and the largest by a 3 horsepower one.

Burners

The coal usually drops from the feeder into what is known as the "burner" or injector. This in its simplest form is shown in Fig. 103 and consists of a short cone within a tube. The coal is

usually fed into the injector at a point just behind the small end of the cone. The air enters the larger end of the cone and issues in the form of a jet from the smaller end. The sudden expansion

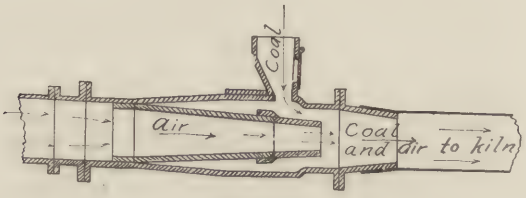


Fig. 103.

of the air as it leaves the jet causes a partial vacuum in the space behind it, with the result that air is sucked into the tube through any openings placed behind the apex of the cone. Usually only a part of the air is blown through the nozzle of the inner cone, the balance is sucked in with the coal. This secondary

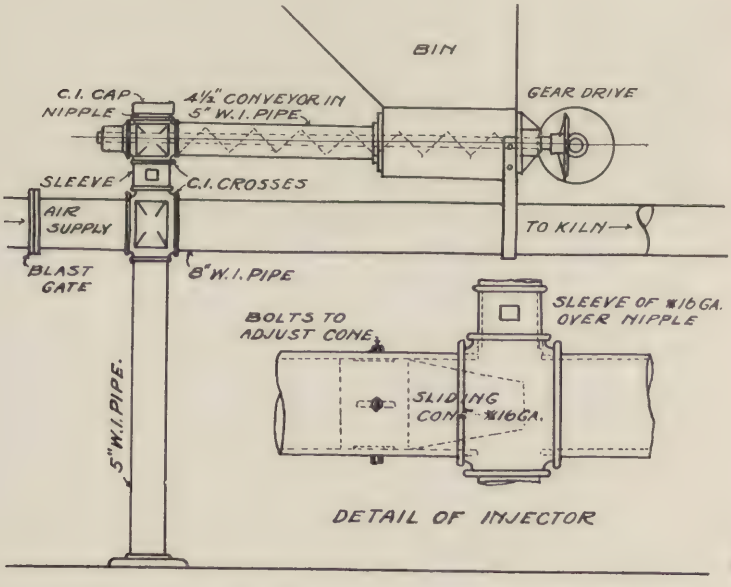


Fig. 104.—Burner and injector made of standard pipe fittings.

air can be very readily controlled by means of a shutter or register. The best place to admit this secondary air is where the coal drops down, as this allows the air to mix with the coal and help carry it into the injector.

An arrangement of feeder, injector and fan employed by the writer for rotary kiln heating is shown in Fig. 104. It is made of standard pipe fittings and parts. The worm is a piece of half pitch screw conveyor and the extension of this beyond the bin is encased in a piece of ordinary wrought iron pipe. The bearings are made of cast iron and bolted on the pipe flanges. The worm is driven by a variable speed motor through an encased worm gear. When a motor can not be conveniently used, the disc and wheel arrangement previously described is used. The injector is made of standard pipe fittings and consists of a cross-tee which the air cone fits as indicated. The upper branch of the cross receives a nipple which connects with the coal feed. The branch below this receives a pipe which rests on the floor and serves to help support the burner, while the fourth branch connects with the furnace. Air is admitted above the coal feed. If more air is desired it may be admitted back of the air cone.

Steam and High Pressure Air Burners

Occasionally injectors are operated by means of steam or compressed air and Fig. 105 shows an injector suitable for this purpose. (An injector similar to those shown in Figs. 103 and 104 except that a steam pipe takes the place of the cone described above may also be employed).

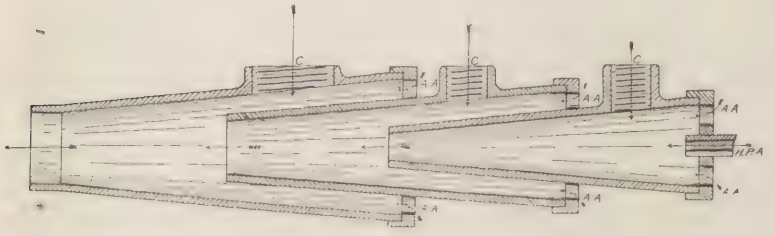


Fig. 105.—High pressure coal burner.

The high pressure burner shown consists of a series of cones placed one within the other. The orifice of each cone being somewhat larger than the preceding one. High pressure air or steam at 60 to 80 pounds is led into the first cone at HPA. As it expands it sucks a portion of air through the openings AA. As it leaves the first cone it expands again sucking a further portion of the air through the openings BB. As it leaves the second cone and enters the third one, it expands a third time sucking a third portion of the air through the opening CC. Coal is fed through the openings D1, D2 and D3, from a worm feeder above similar to that employed for the low pressure burner. In this burner the great difficulty is, of course, to so proportion the coal that each opening will deliver some to the burner. The difficulty of doing this will be appreciated. It is much more expensive to operate a burner with high pressure air than with air from a blower so that these high pressure burners are not now used to any great extent.

Where steam is employed a large volume of air is sucked into the burner and this air is really the carrying medium for the coal.

Charles A. Matcham, manager of the Lehigh Portland Cement Company in 1908 took out a patent on a method of introducing pulverized coal into the cement kiln by means of the draft of the latter. His "natural-draft" system consists in feeding the coal from a bin by means of a worm in a thin sheet across a slit in the hood or end housing of the kiln. Air sucked in by the draft of the kiln through this slit picks up the coal here and carries it into the kiln. No fans or blowers are required and the necessary draft is secured by means of a stack of the proper height. This system was never used to any extent in the cement industry.

Another burner which was developed for cement is that devised by W. R. Dunn, superintendent of the Vulcanite Portland Cement Company. This burner is intended to give a more intimate mixture of air and coal than is secured by the ordinary feeders. In order to secure this result, instead of dropping through one opening in the bottom of the conveyor trough, the coal falls through a number of such openings, while air is sucked

in above and passing down through these openings mixes with the fuel.

Practically all of the firms making a specialty of pulverized coal installations have developed burners. Most of these are modifications of the standard cone and worm with some additional features designed to regulate the air supply or to give better mixing of the air and coal.

Unit System and Aero Pulverizer

The Unit system, in which the coal is pulverized and blown into the furnace by one machine, has been employed to a very limited extent in the cement industry, The general impression seems to be that the system is inefficient as regards power and repairs and does not grind the coal fine enough. This is not borne out by the writer's experience. So far as power consumption and repairs go an installation of Aero Pulverizers will operate as economically as will a central station plant, when power required to transport and blow the coal into the furnace is also considered in connection with the latter. These pulverizers will also grind coal sufficiently fine for cement burning, where a fineness of 90 per cent passing the No. 100 mesh sieve is sufficient, and no economy can be shown by pulveriizing any finer than this.

The unit pulverizers require no dryer unless the coal is very wet. They show better efficiency as regards power if fed with dried coal, however. The best known unit pulverizer is the Aero. This consists of three or more communicating chambers, (Fig. 106), each slightly larger in diameter than the preceding one. A series of paddles mounted on discs, which are in turn keyed to a central, horizontal shaft, revolve in each chamber. An additional chamber at the end of the pulverizer nearest the furnace contains a fan the function of which is to blow finely pulverized coal and air through a pipe to the furnace. The communicating chamber provides the air separation within the unit and an adequate control of the fineness.

The coal is fed into the pulverizer by means of an automatic feed. Some air is also admitted with the coal through inlets in

the feeding device. An additional supply of air can be admitted at a point just preceding the fan chamber and the regulation of the air supply used for combustion is usually effected at this

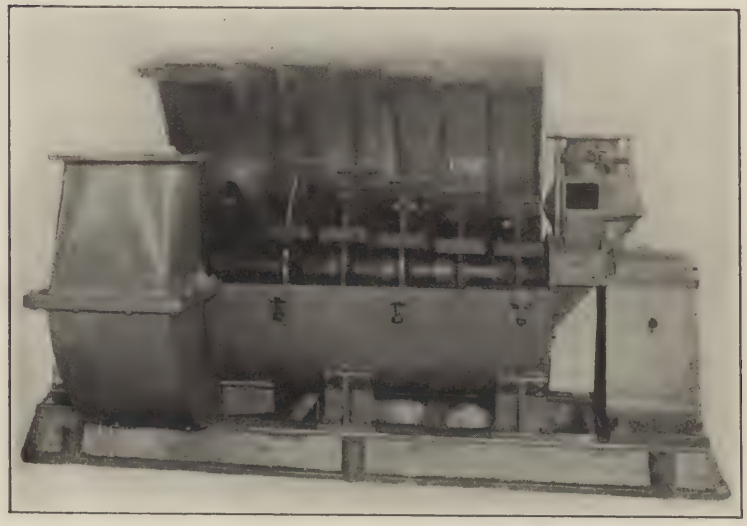


Fig. 106.—Aero pulverizer with cover lifted.

point. The pulverizer runs at a constant speed and the supply of coal burned in the furnace is regulated at the feed mechanism of the pulverizer.

One of the outstanding advantages of the aero-pulverizer is the uniform mixture of air and coal obtained in the fan chamber. The thoroughness of this mixture determines more than any other factor the ability to burn coal efficiently, whether coarse or fine. Fuel engineers now generally agree that a uniform mixture of air and coal is fully as important as fineness of the latter and repeated tests which have been made by the Bureau of Standards and other users of pulverized coal indicate that when the mixture of coal and air is complete and the furnace of proper design, moderately coarse coal is burned as efficiently as the fine product.

Owing to the fact that the operation of the furnace is dependent on the pulverizer being in operating condition, it is highly desirable that repairs can be quickly made. The parts most subject to wear are the paddles and liners. The latter have a comparatively long life and the replacements most often necessary are the paddles, hence it is well to provide close at hand an extra rotor with paddles attached, so that repairs can be rapidly effected. The time required to make the change from the old to the new rotor need then not exceed 20 minutes.

These pulverizers are made in a number of sizes ranging in capacity from 600 pounds of coal per hour to 5,000 pounds. The horsepower required varies from 10 horsepower for the smaller size to 60 horsepower for the one of largest capacity. Table XXXVI gives the makers' figures as to size, capacity and normal power consumption of the various sizes of this mill.

TABLE XXXVI.—CAPACITY AND POWER CONSUMPTION OF AERO COAL PULVERIZERS.

Size	Capacity	Normal power consumption
A	600	10
B	1,000	14
D	1,800	25
E	3,000	40
G	5,000	60

The most recent installation of Aero pulverizers in a cement mill is in connection with the new plant of the National Cement Company, Montreal, Fig. 107. In this plant, there are three kilns, 9 feet by 160 feet, dry process. Each kiln has its own aero pulverizer, the Size G being used. This size is good for 5,000 pounds of coal per hour. In order to faciliate repairs, an I-beam passes over the mills so that the rotors and liners can be easily replaced, a spare rotor and paddles being kept on hand for this purpose. A fourth aero with its motor is also mounted on a truck. This truck moves on a track behind the row of regular pulverizers. In case of accident to one of the latter or its motor, the spare pulverizer is moved into position and connected up with the kiln. This can be done in a few minutes thus avoiding any shutdown.

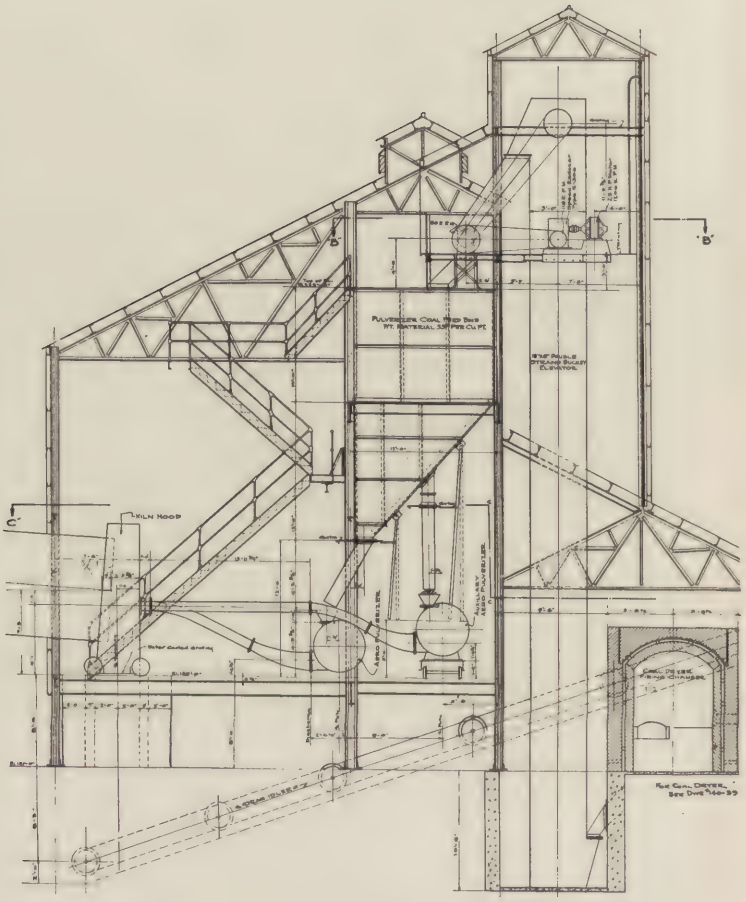


Fig. 107.—Arrangement for heating kilns with aero pulverizers—National Cement Co., Montreal, Que..

The aero can be best driven by means of direct connection through a flexible coupling to a motor of the proper speed.

Storage of Coal.

Cement plants are required to keep on hand a considerable amount of coal in order to have a steady supply independent of car shortages, transportation tie-ups, strikes at the coal mines, etc. Slack coal is also somewhat cheaper during the summer months than in the winter and many consumers purchase and store a large part of their yearly requirements in the former season. Coal is generally handled in the newer cement works by a locomotive crane equipped with a clam shell bucket. In the older plants, a trestle with or without underground conveyors is sometimes employed. There is some risk of fire in storing coal in open piles.

O. A. Done, writing in *Engineering News,* gives the following hints on the prevention of spontaneous ignition in coal piles. The amount of moisture in a bituminous coal is a measure of the risk of spontaneous combustion when the fuel is stored. Bituminous coal should not contain more than 4.75 per cent water. Coal bins should be of steel or iron protected by concrete and should be roofed over. Free air passages should be provided around the walls and beneath the bins to keep the pile cool, and the depth of the coal should never exceed 12 feet. It is useless to provide air passages in the body of the pile as these only tend to promote oxidation. Hence cracks, etc., in the walls of the fuel bin increase the risk.

Oil

Oil is employed where it can be obtained more cheaply than coal. This is an excellent fuel easily employed and free from ash. Oil is burned by spraying it into the kiln with air or steam. The apparatus employed generally consists of an atomizer or burner where the oil and air are mixed, a pump for supplying the burner with oil and a source of air. The burner is merely an adaptation of the common atomizer of the drug store and is shown in its

simplest form in Fig. 108. The burner shown here is designed for use with compressed air and consists of internal pipe through which the oil passes, an external pipe through which the air is forced. The air and oil meet at the orifice of the pipe and

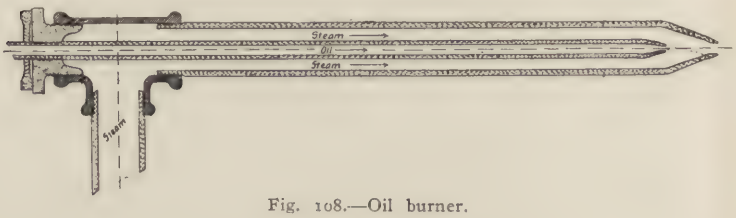


Fig. 108.—Oil burner.

leave the latter in a mist or spray which in turn is mixed with more air in the kiln.

Where the oil is very viscid it is necessary to heat it in order to make it flow easily so that it can be atomized. Steam coils

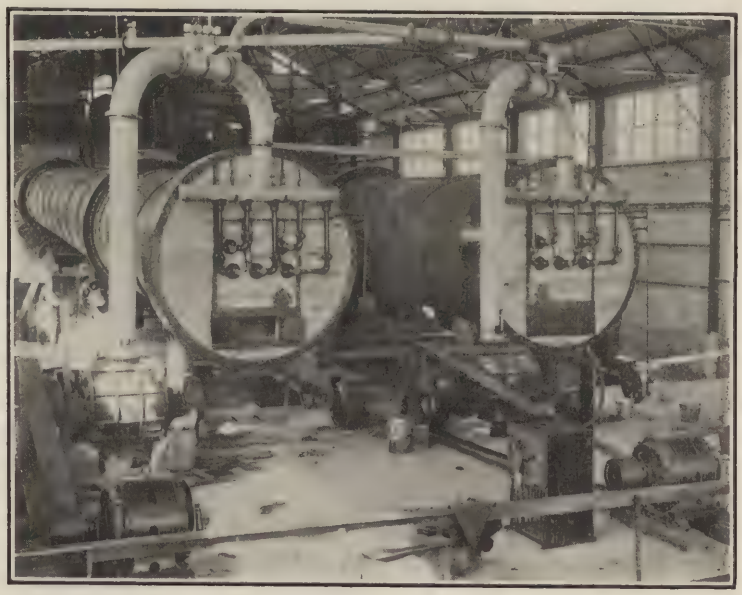


Fig. 109.—System for burning oil—Great Western Portland Cement Co., Mildred, Kans. (Kilns and blowers driven by Wagner Electric Co. motors.)

are often placed around the exit pipe in the storage tank when the oil is so viscid that it will not flow out of this. With most oil, however, such a coil would only be used in cold weather. It is the general practice to heat the oil before it goes to the burner, however, and this is usually done by means of regular oil heaters similar to feed water heaters in which the heating is done by the exhaust steam from the pumps or else by live steam. Occasionally the heat of the clinker is made to do this work by placing a coil of the oil supply pipe at some point where the heat radiated from this can reach it. At one of the western plants a coil of pipe was placed in the hood and the oil so heated just before it reached the kiln.

Fig. 109 shows an installation of oil burners on a kiln. It will be noted that a number of burners are employed. This is the general practice—to use a number of small burners rather than one large one.

Burning with Natural and Producer Gas

Natural gas has been successfully used for the heating of the kiln, both in the Kansas field and at Wampum, Pa. At the plant of the Iola Portland Cement Company, Iola, Kansas, the gas was also used in gas engines to generate power for grinding, etc. Producer gas has been tried but the writer knows of but one plant where it was used for any great length of time, that was at a small plant in Canada. In conversation, the manager of this plant informed the author that they considered it as cheap as powdered coal, but saw no particular advantage in its use. The question has been raised at numerous times as to whether sufficient heat could be developed by its use to secure the proper temperature in the kiln for burning, and numerous calculations have been given to prove that without regeneration producer gas could not be used for burning Portland Cement. The fact that it has been used at several plants should effectually set at rest this contention. The temperature required for cement

burning has been placed too high, however, and the gas considered as cold in most of these calculations, whereas it is usually introduced hot from the producer into the kiln.

The Diamond Portland Cement Company, Middle Branch, O., at one time had a Swindell gas producer in operation heating one of their kilns, but have now discontinued its use. Fig. 110. shows the installation of the producer at this plant. The gas producer was built 15 feet in front of the kiln, which was 6 feet in diameter and 60 feet long. The coal, which was of inferior

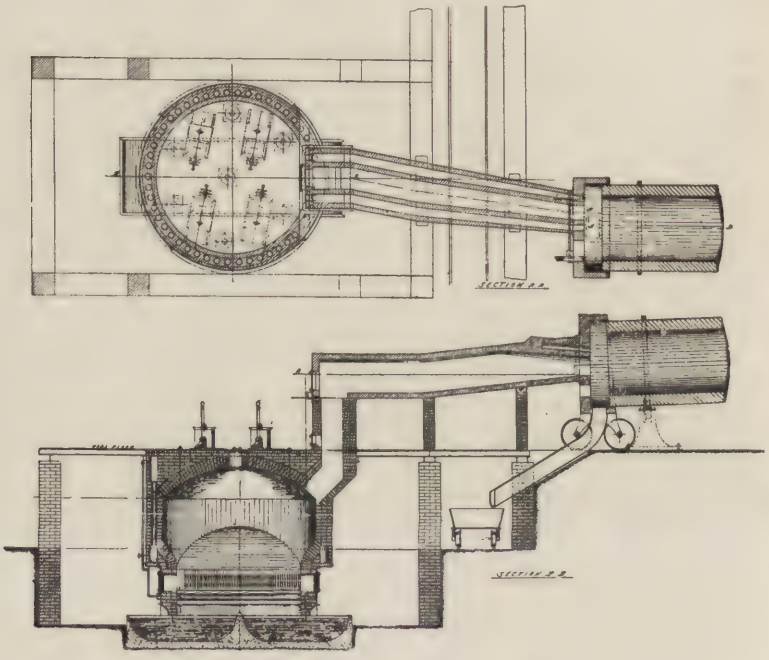


Fig. 110.—Swindell gas producer and rotary kiln.

quality and cost only $1.50 per ton was introduced into the producer by means of sliding hoppers. Steam and air were introduced under and through the inclined grates by means of blowers. The air used for combustion was preheated by passing up through iron tubes built in the walls of the producer.

The air and gas were led to the kiln by separate flues as shown in the plan. The labor required to operate the producers amounted to about 3½ cents per barrel of cement including the wages of the burners, the coal consumption amounted to 130 pounds per barrel and the output to 240 barrels per day. In order to properly clinker the materials, it was found necessary to add soda ash to the mix to lower the clinkering temperature to a point which the producer gas could reach. This installation of producers was here found unsatisfactory and was finally replaced by coal burning and pulverizing apparatus.

Mr. H. F. Spackman, in a paper read at a meeting of the Cement Manufacturer's Association, stated that in a plant designed by his company, producers were tried in connection with powdered coal on two rotary kilns, 60 feet long by 5 feet in diameter, burning slurry containing 60 per cent water. Actual figures in this plant obtained on a two or three months' run, were 125 barrels of cement per day, with a coal consumption of 135 pounds of coal per barrel, while the kilns working on powdered coal required on an average for a seven months' run 138 pounds of coal per barrel. To greatly overbalance this 3 pounds saving in coal, however, was the fact that six men each shift of twenty-four hours were required to work the producers and that as gas slack could not be employed a coal costing 50 cents a ton more had to be substituted.

All attempts to burn cement by producer gas were confined to a period about fifteen years ago and the writer knows of no plants which are at the present time employing it. Powdered coal has the disadvantage over gas firing in that the inherent losses of the gas producer are overcome. These losses are by no means small. It is estimated that the average loss of heat in the gasification of fuel, due to complete combustion to carbon dioxide, heat radiation, etc., is seldom less than 20 per cent. If to this is added the loss due to the carbon which the ash carries away with it and the coal consumed in the boiler for the production of the steam

required for the gas producer, it is safe to say that the loss may generally be considered as 30 per cent of the thermal value of the coal.

Furthermore, with gas firing the ashes have to be handled and disposed of while with pulverized coal the ash is blown away or enters the clinker. No advantage can be claimed for gas firing which can not also be claimed for coal except the doubtful one of the contamination of the cement by the ash. As was shown in a preceding section, about half the coal ash goes up the chimney and it is very doubtful if what falls down into the mix does not form hydraulic compounds with the lime of the latter. It is certain that it does combine with the lime as is shown by the fact that practically all cement is soluble in dilute acid, while coal ash is insoluble. If, therefore, the ash did not combine, a residue of at least one-half per cent would be left when cement is treated with dilute acid.

Another advantage claimed for producer gas is the ease with which the flame can be regulated. Analyses of the flue gases of the kiln show combustion to be complete with about 20 per cent excess air which is as good as could be expected with producer gas. Furthermore, pulverized coal is of almost constant composition throughout long periods while the composition of gas varies with the operation of the producers, etc.

Coal can be pulverized for less than it can be gasified, the labor of handling the producers alone amounting to more than it costs to pulverize coal. The cost of pulverizing coal rarely amounts to more than 3 cents per barrel of cement burned and often falls below this.

Natural gas is found in too few localities to make it generally applicable to cement burning, and, even when found, the supply is limited and may give out after a few years. Below are analyses of the gas at Iola, Kansas, and at Independence, Kansas, at both of which places Portland cement mills used nat-

ural gas not only for heating the kilns but also for generating power.

ANALYSIS OF NATURAL GAS USED FOR BURNING PORTLAND CEMENT IN KANSAS (BAILEY).

	Iola	Independence
Hydrogen	0.00	0.00
Oxygen	0.45	trace
Nitrogen	7.76	3.28
Carbon monoxide	1.23	0.33
Carbon dioxide	0.90	0.44
Ethylene series	0.00	0.97
Marsh gas	89.66	95.28

CHAPTER XIV

COOLING AND GRINDING THE CLINKER, STORING AND PACKING THE CEMENT, ETC.

Cooling the Clinker

The clinker leaves the kiln at a temperature of about 2,100° F. It is, of course, entirely too hot to grind and must be cooled. It has generally been found preferable to do this mechanically instead of letting the clinker lie in heaps and cool of itself. In some mills this has been done in the open air, in others in rotary coolers, while a few of the older mills still use the upright cooler shown in Fig. 111. This consists of an upright steel cylinder about 8 feet in diameter and 35 feet high provided as shown with baffle plates and shelves. As the clinker falls over these it meets a current of air blown in through a perforated pipe running up through the center of the cylinder and is thus cooled. There is usually one cooler to each pair of 60-foot kilns or to one 7 by 100-foot kiln. Larger coolers are also employed for bigger kilns. The clinker is led from the kilns by chutes to a bucket elevator which carries it to the top of the cooler. The clinker is usually drawn from the bottom of the cooler on to belt conveyors, or else into barrows and carried to an elevator, whch carries it up to the bins above the ball mills or rolls, whichever are used to grind the clinker.

Usually water is added to the clinker in a steady stream as it falls into the elevator pit. This helps to cool the clinker, makes it more brittle and easier to grind and saves the elevator from handling such very hot material. There is probably no action toward curing of the cement or hydration of the free lime, since any of the latter present is usually locked up in the interior of the clinker.

The writer has frequently cooled clinker suddenly by plunging it, red hot from the mouth of the kilns, into water. The only perceptible effect is to bleach the color from dark greenish black to nearly white. If this clinker is dried and ground, it will be

found to have pretty much the same properties as clinker caught at the same time and allowed to cool slowly in air. The writer has never observed that unsound cement could be made sound by this process. It does take up some water (probably on the

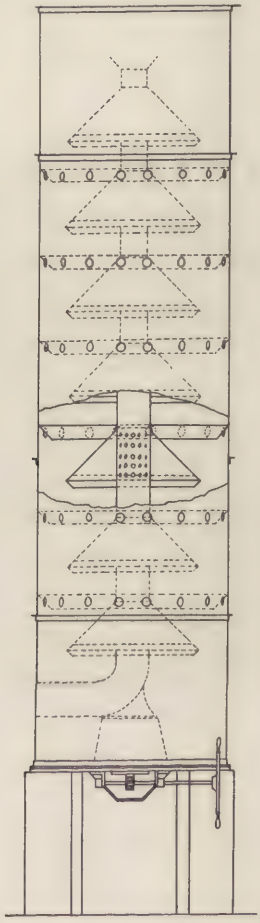


Fig. 111.—Upright clinker cooler (Mosser & Son).

outside of the lumps only, however), as a loss on ignition test will show. Such clinker is easily ground and the resulting cement trowels nicely.

The more modern mills employ a rotary cooler (see Fig. 112) which consists of a steel shell similar to that of the kiln and mounted on carrying rollers just as the kiln is carried. Usually this is lined with cast iron plates which are bolted in, so that they can be easily removed. Occasionally, however, the coolers are lined with fire brick or vitrified brick. One cooler is generally employed for each kiln, the cooler being located below the kiln to

Fig. 112.—Rotary cooler—Great Western Portland Cement Co., Mildred, Kans., (Driven by Wagner Electric Co. motors.)

permit of the discharge of the hot clinker directly from the kiln into the cooler by means of a chute. The air for cooling is drawn in by the draft of the kiln, and, as the air passes from the cooler to the kiln, such coolers act as preheaters for the air entering the kiln. As every pound of clinker carries out of the kiln between 400 and 500 B. t. u., it will be seen that this practice should save some coal.

The cast iron lining plates are often made T-shaped so that when they are inverted and bolted in the kiln they will form shelves running lengthwise with the latter. These shelves act as carriers, lifting the hot clinker and dropping it through the current of air. Sometimes the coolers are lined at the feed end only, the balance of the shell being unlined but usually provided with angle irons or Z-bars fastened to the inside of the shell to serve as lifters. Water is sometimes fed in at the upper end of the cooler to help cool the clinker.

At the discharge end of some of these coolers, for about 3 feet, the shell is perforated with holes from 1¼ to 2 inches in diameter, while at the end itself is a large angle iron with the flange turned in so as to hold inside of the coolers any large lumps of clinker which do not pass through the holes, making a rotary screen out of the lower end of the cooler. The large lumps may be broken up by an attendant with a bar or hammer, or else several large balls may be placed in the cooler and allowed to roll around in the latter, thus serving to break up the large pieces of clinker. This form of screen cooler, we believe, was first introduced at the plant of the Louisville Portland Cement Company, Speeds, Indiana but it has since been adopted at a number of mills.

Occasionally rotary coolers are mounted separately from the kilns so that the air from the former does not pass into the latter. This is usually done where the lay of the land will not allow excavating for the coolers. When so located the clinker is carried from the kilns to the cooler by means of a bucket elevator and the air for cooling may be either drawn through the coolers by means of a stack at the upper end or else blown in by a fan. The question of the thermal advantage gained by allowing the air employed for combustion to enter the kiln has received considerable attention by cement mill engineers and there seems to be some uncertainty in the minds of these as to the benefits to be derived from the practice. Theoretically a barrel of clinker (380 pounds) leaving the kiln at 2,000° F. above atmospheric temperature should carry out with it, $380 \times 2{,}000 \times 0.246 = 186{,}960$ B. t. u. This is equivalent to about 13.4 pounds of coal.

If all of this heat could be applied to the work to be done, the use of the cooler would save this amount of fuel. Unfortunately, only 20 to 35 per cent of the thermal value of the fuel is utilized in burning the cement, the balance is wasted in various ways as explained in Chapter XII. Some of the heat carried out of the kiln by the clinker is not transferred to the air entering the kiln but instead is lost by radiation from the cooler shell. In the case of a metal-lined cooler from 30 to 40 per cent of the heat of the clinker is so lost. Of the 150,000 to 200,000 B. t. u. carried out of the kiln by the clinker, therefore, only 90,000 to 140,000 B. t. u. is employed in heating the air entering the kiln.

Assuming 100 pounds of coal (14,000 B. t. u.) are required to burn a barrel of cement, or the equivalent of 1,400,000 B. t. u., of which only about 280,000 B. t. u. or 20 per cent are employed in doing work, it will be seen that by adding 90,000 to 140,000 B. t. u. we have increased the thermal input of the kiln by from 6½ to 10 per cent or to 1,540,000 B. t. u. per barrel. This should burn, therefore, from 6½ to 10 per cent more cement from the same fuel.

When tests have been conducted with rotary coolers and the preheated air used the coolers have generally effected a saving of from 5 to 7 pounds of coal per barrel of cement burned.

The capacity of a rotary cooler will depend much on the installation, particularly as regards the flow of air through it and the lifting of the material. Efforts should be made to arrange the cooler so that practically all the air needed for combustion, aside from that used for blowing the coal should pass through it. Under such conditions the capacity of various sizes of rotary coolers is as follows:

TABLE XXXVII.—Capacity of and Power Required to Operate Rotary Coolers

Size	Capacity per day Bbls.	H. P.
5 ft. diam. x 50 ft. long	425	7½-10
6 ft. diam. x 60 ft. long	800	10-15
7 ft. diam. x 70 ft. long	1,350	15-20
8 ft. diam. x 80 ft. long	2,000	25-35

The capacity of the cooler can be materially increased if water is employed at the feed end. When the air from the cooler enters the kiln, however, there is an objection to the steam which tends, if present in too great quantity, to cool the kiln.

The clinker usually drops from the coolers on to belt or pan conveyors, which carry it to the clinker grinding department or else into storage.

Utilization of Heat in Clinker for Other Purposes than Preheating Air for Kiln

One of the New York state mills, at one time, used a cooler which consisted of a water-jacketed revolving cylinder, the water entering and leaving the jacket through pipes leading from a specially designed feeder placed in the center of the discharge end of the cooler. The water after leaving the cooler was used in the boilers, the cooler simply acting as a feed-water heater. These coolers are said to have worked well, and to have cooled the clinked perfectly.

The employment of the heat in the clinker in this manner does not seem to promise much in view of the fact that there is usually about the power plant itself sufficient waste heat in the exhaust steam from pumps, etc., or in the stack gases to take care of the boiler feed water. The heating of this latter in a feed water heater or an economizer of the Green type is manifestly a much simpler undertaking than in a rotary cooler and the apparatus itself is less complicated and apt to get out of order. There is also the objection to connecting together two such dissimilar operations as cooling clinker and heating feed water.

At one or two mills, the hot air from the cooler is passed through a rotary dryer and used to dry the coal. There is no objection to this practice except that the coal dryer is often so placed that a long flue would be necessary to connect the cooler with the dryer. From the score of both efficiency and safety in coal drying the practice is admirable, as the air from the cooler is always much below the temperature at which coal ignites and the large volume of warm air is a most effective dry-

ing medium. The drying of coal seldom requires more than 30 pounds of coal for firing the dryer per ton of coal dried or about 1½ to 2 pounds of coal per barrel of cement. The utilization of the heat in the clinker in this manner, therefore, would not seem to be as desirable as in the kiln where a saving of from 5 to 7 pounds of coal should be effected. It would, however, at many plants be an easy matter to employ the air from one or two coolers as might be required for drying the coal and the air from the balance of the coolers in the kilns. In this way, the entire quantity of heat in the clinker could be utilized. To those who are interested in such a system the Randolph Dryer[1] should appeal, as this is especial designed to make use of warm air of low temperature, such as boiler stack gases, in drying coal.

Storing and Seasoning Clinker

Cooling clinker in pits has been tried at a number of places, but does not seem to have worked very well anywhere. Some few mills convey their clinker red hot out into the fields and allow it to cool naturally. This is usually done at plants employing some form of crane for the handling and storage of clinker. The usual practice at such plants is to drop the hot clinker from the kiln into some form of pan or chain drag conveyor and convey the material outside the building, depositing it upon a pile or into a pit. Water is usually added at this point, although it is sometimes sprinkled on the clinker as the latter leaves the kiln or moves along on the conveyor. The crane handles the clinker from the pile or pit and carries it out into the storage, spreading it in layers so as to allow it to cool. This action is materially assisted by sprinkling the pile with water from a hose.

Until quite recently it was very generally believed that seasoned clinker, provided it is dry, grinds much more easily than clinker fresh from the kilns, the slaking of the free line no doubt serving to help break down the structure of the material. In order to take advantage of this fact, mills which cool their clinker by means of one of the mechanical devices described above have installed systems for seasoning their clinker. By cooling the clinker first

[1] Fuller-Lehigh Company, Fullerton, Pa.

it is much easier handled as belt conveyors can be used to replace the more troublesome pan and apron conveyors necessary for the hot material, and also if rotary coolers are used the heat in the clinker may be utilized to heat the air entering the kiln, whereby fuel will be saved.

The arrangements provided for the seasoning of the clinker are, of course, intended to pile this economically and in large quantity and then to reclaim as much of the pile as possible automatically and with a minimum of labor. The first systems employed consisted of pan or belt conveyors, but all of the recent clinker handling systems make use of some form of crane and grab bucket, using the latter both for conveying the clinker into storage and for reclaiming it when it is ready to grind.

One of the first mechanical systems for seasoning clinker was worked out by Mr. Owen Hess and the author for the Dexter

Fig. 113.—Clinker storage—Dexter Portland Cement Co., Nazareth, Pa.

Portland Cement Company, at Nazareth, Pa. (Fig. 113). This storage consists of a pan conveyor which is supported on a

steel trestle and protected by a roof. The conveyor may be discharged at fixed points. The clinker is carried out and deposited underneath this conveyor in a long pile. It is allowed to remain here two or three weeks, when it is drawn out by means of spouts on to belts in two underground tunnels, which run lengthwise under the clinker piles. No roof is placed over the clinker and any rain which falls upon it helps to season it. Owing to the fact that in very rainy weather this clinker when drawn from the pile is wet, it was deemed advisable to install a dryer just before the grinding mills, but this dryer was only used occasionally when the clinker was very wet and finally was removed altogether. The capacity of the storage is about 72,000 barrels of clinker. The clinker is drawn out of one end of the pile while it is being dropped into the other.

Traveling Crane for Handling Clinker

The most popular system for handling clinker is unquestionably the overhead electric traveling crane and grab bucket (Fig. 114).

Fig. 114.—Clinker handling bridge crane, 80 ft. span, at the Bath Portland Cement Co., Shepard Electric Crane and Hoist Co., maker.

This will handle hot or cold clinker and may be made to cover practically any desired area. The traveling crane consists of a

bridge composed of two parallel I-beams or plate girders which travels on two parallel rails supported at an elevation from the ground. The rails may be supported by an "A"-frame or in any appropriate manner. When the clinker storage is in the form of a bin, the rails may be supported on the side walls of the bin. The bridge is propelled by means of a motor located at some convenient place on it which is controlled from the operators cage. This motor actuates through gearing a shaft parallel with the bridge, which in turn revolves the wheels on trucks at the two ends of the beam. There operates back and forth on the bridge a trolley upon which are located three drums which in turn lower, open, close and raise the grab bucket. The trolley and drums are operated by suitable motors, controlled from the operators cage, usually located at one end of and below the bridge. With this crane it is possible to deposit and reclaim clinker at any point over which the bridge moves. The dimensions of the crane, of course, depend entirely on the size and shape of the clinker storage and the amount of clinker to be handled. The buckets usually hold from 2 to 5 cubic yards of clinker. The bridge beams is generally from 60 to 120 feet long. A 5-ton crane will handle a 2-cubic yard bucket and a 10-ton crane a 4-cubic yard bucket.

The clinker storage of the new National Cement Company's plant at Montreal-East, Quebec, is a good example of such a storage. This storage takes clinker direct from kilns and has a 5-ton bridge crane[1] of 100-foot span equipped with a 2-cubic yard bucket. The storage itself is 255 feet long. The area covered is 25,500 square feet. The supporting track is 45 feet from the ground and the capacity of the storage 225,000 barrels of clinker. The bridge itself has a maximum travel of 300 feet per minute, the trolley travels at a speed of 125 feet per minute and the hoisting at 100 feet per minute. It will handle 3,000 barrels of cement daily in and out of storage.

[1] Shepherd Electric Crane and Hoist Company, Montour Falls, N. V.

Revolving Cranes for Handling Clinker

At the plant of the Bessemer Limestone and Cement Company a stationary crane is employed (Fig. 115). This crane was made by the American-Terry Derrick Company, and is known as a full circle crane. It is mounted on a concrete foundation 25 feet

Fig. 115.—Full circle crane—Bessemer Limestone and Cement Co., American Terry Derrick Co., maker.

high and located in the center of the storage pile. As its name implies the boom which is 100 feet long moves over the entire radius of the pile and handles a 3-cubic yard clam shell bucket. The main hoists are equipped with 100 horsepower motors and the swinging hoists with 30 horsepower motors. This storage has a capacity of 150,000 barrels.

Figure 116 shows the form of crane employed by the Pacific Portland Cement Company. This crane also swings in a circle over a circular pile. The effective radius of the crane is 80 feet while the distance from the bottom boom to the guy cap is 50 feet.

Fig. 116.—Clinker storage and crane—Pacific Portland Cement Co., American Hoist and Derrick Co., makers.

The crane is supported by six 1-inch steel guy ropes each 240 feet long. The entire machine is operated by one 35 horsepower motor operating at 900 revolutions per minute. The crane is equipped with a 40-cubic foot Brownhoist clam shell bucket.

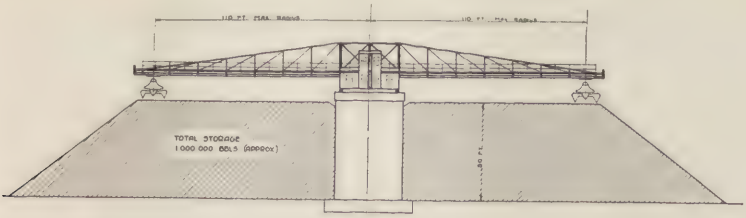


Fig. 117.—Clinker storage—Riverside Portland Cement Co., Brown Hoisting Machine Co., makers.

Still a fourth type of clinker handling crane is shown in Fig. 117. This shows the clinker storage of the Riverside Portland Cement Company, Riverside, Cal. The double contilever full

circle rotating crane employed here has an effective radius of 110 feet. It is mounted on a hollow reinforced concrete tower, 55 feet high and 34 feet in diameter. Entrance to the tower and crane is through a tunnel under the clinker pile. The clinker is handled by means of two 60 cubic foot buckets—one on each arm. The effective height of the storage is 50 feet and this gives a storage of about one-half million barrels, allowing for reduction of the pile by buildings, etc., which cut into the storage. The bucket hoisting and closing motors are each 25 horsepower, the trolley travel motors 15 horsepower and the motor for the rotating mechanism 50 horsepower.

At the above plant, the twelve rotary kilns dump into a McCaslin conveyor, which in turn conveys the clinker into storage, discharging it at a height of 35 feet at a point passed over by the extreme ends of the crane arms. The clinker is removed from this discharge pile and deposited in any desired space within the swing of the crane by the buckets. Reclaiming is effected by taking it from the desired part of the storage and dumping it over a reclaiming tunnel. The latter extends under and partly through the storage and is provided with spouts and a 24-inch belt conveyor which carries the clinker to the finishing mill. One operator can handle both buckets and distribute 6,000 barrels in storage and reclaim a like amount daily.

Properties of Seasoned Clinker

As has been intimated damp clinker is difficult to grind. Dryers are not, however, placed after the storage as a general rule. Sometimes a roof is placed over the storage but more often the pile is simply exposed to the rain and snow. In which case, during wet weather only fresh clinker is ground, allowing the pile to dry itself by the absorption of the water by the lime of the clinker or by evaporation during clear weather. With the crane, the clinker may be dried when it is not actually raining or snowing by mixing damp clinker with hot clinker. At some mills, it is, therefore, the practice to spread a layer of hot clinker on the floor of a part of the storage and then a layer of damp clinker

on top of this and then when the latter is dry and the former is cooled, the mixture is ground. At the plant of the National Cement Company, previously mentioned, the drying of the seasoned clinker is effected by mixing some hot clinker with this and passing the two through a rotary dryer. No fire box is to be used for the latter and the heat in the fresh clinker is utilized in evaporating the moisture in the seasoned material.

Clinker which has been seasoned has absorbed more or less water and carbon dioxide, the quantity usually amounting to from 2 to 4 per cent, depending on the length of time of exposure and atmospheric conditions during this period. The effect of this seasoning is to improve the soundness and trowelling properties of the cement. Seasoning always, however, lowers the specific gravity and often the one and seven day tests of the cement made therefrom.

Generally speaking, it has been found most desirable to grind a mixture of fresh and seasoned clinker rather than seasoned clinker alone. The seasoned clinker, while unquestionably softer, gives off much steam in the mills and the presence of the fresh clinker counteracts this by absorbing this steam. This, of course, in turn results in hydration of the free lime in the fresh clinker and hence to some extent rapidly seasons the latter.

Adding the Retarder.

Before being ground, it is usual to mix with the clinker the gypsum necessary to retard the setting time of the cement (see Chapter XXI). The gypsum is usually received at the plant in the form of small lumps, crushed to pass a one-inch ring screen. In most plants the retarder is added by hand although at a few, automatic scales are used. The latter have not always proved successful, the usual trouble being the small amount of gypsum (2-3 per cent) added to the clinker and the difficulty of getting automatic scales which will handle a few pounds of such lumpy material simultaneously with several hundred pounds of clinker.

At the older plants where the clinker is wheeled from the coolers to the grinding department the gypsum is usually added

to the barrow and the amount added is determined by volume and not by weight. A shallow box holding the desired amount of gypsum is used and this is filled with gypsum and struck off level with the top. This answers the purpose very well and serves to control the gypsum in the cement within narrow limits. When belts are used to convey the clinker, these usually dump into a hopper scale. This latter may be either automatic or hand controlled. An attendant adds the gypsum, by means of a box which holds the correct weight of gypsum for one dump of the scales. The scales if automatic are usually provided with counters or if operated by hand the attendant keeps tally on a board so that an account of the amount of clinker ground may be kept.

At one time plaster of Paris was employed to slow the setting time of cement but since the writer pointed out in the first edition of this work that gypsum was fully as efficient a retarder as plaster of Paris and as it costs much less, the former has almost entirely taken the place of the latter. At one time also, Nova Scotia gypsum was almost universally used as it contains a higher percentage of sulphuric anhydride than the native gypsums. Now the cheaper American mineral has replaced the imported one to a great extent. In purchasing gypsum, the manufacturer purchases sulphur trioxide (SO_3) and the consideration with him is usually how much of this he will get for his money.

Grinding the Clinker.

The clinker is ground by any one of the following systems:

SYSTEMS USED FOR GRINDING THE CLINKER.

A. Tube Mill preceded by (*a*) Hercules Mill, (*b*) Ball Mill with screens, (*c*) Kominuter with screens, (*d*) Single roll Griffin Mill, (*e*) three-roll Griffin Mill, (*f*) Kent Mill, (*g*) Sturtevant Mill, (*h*) Huntington Mill, or (*i*) Fuller Mill.

B. Compeb Mill alone.

C. Griffin Mill preceded by (*a*) ball mill provided with perforated plates and without screens, (*b*) Set of crushing rolls, or (*c*) pot crusher. (Often followed by tube mill, see *A.*)

D. Fuller Mill preceded by (*a*) ball mill provided with perforated plates but without screens, or (*b*) set of crushing rolls. (Often followed by a tube mill, see *A.*)

E Kent Mill and (*a*) screen separator (*b*) air separator. (Generally followed by tube mill, see *A.*)

F. Sturtevant Mill and Newaygo separator (Generally followed by tube mill, see *A.*)

G. Huntington Mill preceded by rolls. (Now generally followed by tube mill, see *A.*)

Of these systems the last three so far have found only a limited use. The Huntington Mill both alone and followed by the tube mill is used only by the Atlas Portland Cement Company.

It is usual for the clinker to be ground by the same type of machinery as is used to grind the raw material. The principal reason for this is that only one set of repair parts have to be carried in stock. A number of mills, however, use ball and tube mills to grind the raw materials and Griffin Mills to grind the clinker, the idea of these manufacturers being that the former is the better of the two for soft or wet materials, and the latter the more suited to the hard clinker. The tube mill is also popularly supposed to be a better mixer than other mills but this is not borne out by practice, and the general experience has been that the mill which will grind the raw materials finest will in all cases give the best cement. No mill holds enough material to obtain a uniform mix where this is not secured before the materials reach the mill. The tube mill and Compeb mill are better suited to wet grinding than other mills, and hence are often used in wet process plants for grinding the raw materials even where other mills are employed for clinker.

All of the above mills have been described in Chapter X.

Factors Influencing Grinding of Clinker.

It is now well understood that the percentage of moisture, the

temperature, chemical composition, degree of burning, amount of seasoning, and to some extent the size of the clinker, all influence the operation of grinding cement. The influence of moisture and seasoning has already been noted. Hot clinker grinds much harder than cold clinker and for this reason all clinker should be cold when fed to the mills. The heat resulting from the friction obtained in grinding is itself sufficient to raise the temperature of the cement to 200° to 350° F. If we start with hot clinker, therefore, the temperature finally obtained in the mill is almost sure to be excessive. The loss of output in a mill grinding very hot clinker may be as much as 40 to 50 per cent of one grinding cold clinker, while the power per barrel of cement ground may increase 80 to 100 per cent.

It will be quite evident that the degree of burning must have marked influence on the grinding of cement since by hard burning we may obtain a clinker which is completely vitrified and in consequence of this both hard and heavy. The softer the burning, therefore, the easier the grinding. For this reason it is usual to burn only to the degree of vitrification necessary to produce sound cement. It will generally be found preferable where this can not be obtained by a reasonable amount of vitrification to grind the raw materials finer in order to secure this end rather than to burn harder.

The chemical composition of the clinker has a marked influence on the ease with which it can be ground. Clinker low in iron oxide grinds much easier than clinker high in iron oxide. An increase in the percentage of lime on the other hand makes clinker easier to grind. The writer has frequently stated this, but quite recently Mr. Wm. P. Gano, Chief Chemist, Pennsylvania Cement Company, undertook an extensive series of tests which proved the writer's contention. Gano found for example that, with clinker having a lime ratio[1] of 1.97 a certain tube mill would give 51 barrels per hour; the same mill when grinding clinker having a lime-ratio of 2.10 had a capacity of 68 barrels per hour while with a clinker having a ratio of 2.22 the mill ground 79 barrels. It will be seen, therefore, that the higher the

[1] See page 76.

lime in the cement can be carried, the easier the grinding. Since the power to operate the mill in each case was the same, the power requirements were:

For the clinker with 1.97 lime ratio 5.1 kw-hr.
For the clinker with 2.10 lime ratio 3.85 kw-hr.
For the clinker with 2.22 lime ratio 3.23 kw-hr.

A lime ratio of 2.22 is probably rather high and in this case it might be that much if not all of the power saved on the clinker side would be made up for in increased power necessary for grinding the raw materials fine enough to make a sound cement with such a high ratio. At the same time, a ratio of 2.10 is good practice and it will be noted in Gano's figures that 30 per cent more power was required to grind the clinker with a ratio of 1.97 than to grind one with the higher ratio (2.10). In addition to the saving of power the repairs are, of course, less and there is a saving in interest, etc., on the smaller amount ofgrinding equipment necessary, when a fairly high ratio is employed.

Conveying Clinker and Cement.

The hot clinker, when it is desired to handle this, can best be conveyed by means of pan conveyors, bucket carriers or drag chains. The latter are now considered best. Occasionally drag conveyors are made by fastening a 6- to 10-inch piece of angle iron on to ordinary conveyor chain and allowing these to drag the hot clinker along. The most recent development, however, is an adaptation of the ordinary sawdust or wide link chain, only made much heavier and of special metal designed to withstand heat and abrasion. These operate in a trough the bottom of which is lined with white iron and the material is carried on the upper or lower run of the chain. They are suitable for carrying material on the level or up a slight inclination, say 15 or 20° from the horizontal.

Cold clinker in any form may be elevated by means of any of the standard forms of bucket elevators or conveyed horizontally or up a slight incline on belt conveyors. Fully ground cement is generally conveyed laterally by means of screw conveyors and

the product of the granulating mills (16- to 20-mesh) may be handled in the same way. Inclined belts are sometimes used to both convey and elevate cement.

The Fuller-Kinyon system described for handling pulverized coal is now being used at a number of plants for handling cement This system requires somewhat more power to operate than do elevators, belt and screw conveyors, but its evident advantages such as absence from dust, maintenance and attention required for long lines of screw conveyors, flexibility as regards arrangement, ease of extension to any length desired and in any direction and saving in space required give it the preference over other forms of conveyor yet devised for moving ground cement. Nearly all of the most recently built mills are employing this system for conveying cement from the mill into the stock house bins. One new mill is employing for placing cement from the stock house bins into the packing bins a portable Fuller-Kinyon pump. The latter is mounted on a truck operating on a track under the bins, connection is made with the bin and with the pipe line leading to the packing bin by means of removable connections.

For this purpose the pump is mounted on a car which in turn runs on a track under the silos as shown in Fig. 121. (Refer to page 384). Referring to this *a* is the pump and *b* the motor driving this. The pump is placed directly under the bin opening, *c*, and connection made with the latter by means of clamps and a gasket, *d*, and with the pipe line,*e*, through the hinged connecting pipe, *g*, by the same means. The cement is fed out of the bin by an automatic feeder, *h*, which is driven from the pump shaft. The air gauges *i* are mounted on the car and connection is made with the air line by air hose. The car is kept in place under the bin by suitable track clamps, *k*. One objection to the use of this system here is that two or more pumps are usually required and more room is needed beneath the silos.

Stock Houses.

From the grinding mill the finished cement goes to the stock house. In the early days of the industry this usually consisted

of a long low frame building divided into bins by means of wooden partitions, so that each day's grinding could be kept separate. These bins usually held from 1,000 to 5,000 barrels and were arranged either on each side of a central aisle or else with an aisle on each side. The parts of the bins facing the aisles were stopped up by means of boards which might be easily removed, and below the floor of the aisles, ran screw conveyors to the packing room, which was usually one end or a large room in the middle of the stock house. The screw conveyors were covered with boards, except in front of the bins where gratings 3 or 4 feet in length were placed. The cement was usually brought in from the grinding mills by an overhead screw conveyor, from the trough of which spouts ran to the middle of the bins. The openings in the trough leading into the spouts were closed by iron slides or gates so that the cement might be run into any bin desired at any time. When it was desired to open a bin the bottom plank was removed from the front of the bin and the cement was allowed to run into the screw conveyor, through the grating. When it ceased to run of itself, a scraper, which consisted of a flat iron plate, about 6 inches by 18 inches, from the middle of which a long handle projected was introduced and all of the cement which could be pulled through the opening conveniently was drawn into the conveyor, after which the remainder of the boards were taken down, and the rest of the cement was drawn into the conveyor, either with the scraper or wheeled by barrows to the grating.

This form of stock house was occasionally equipped with cross conveyors which ran across the bins and consequently at right angles to the main conveyors and which emptied into the main conveyors.

To do away with the manual labor required by such a method of opening a bin, stock houses provided with tunnels running under the bins are used. The conveyors are located in the tunnel and the bins are fixed with sloping floors and spouts which deliver into the conveyor. Fig. 118 shows a type of stock house which was installed with various modifications by many of the

mills built between 1900 and 1910. It will be seen that the conveyors are in concrete passage-ways and that most of the contents of the bin can be run out by gravity.

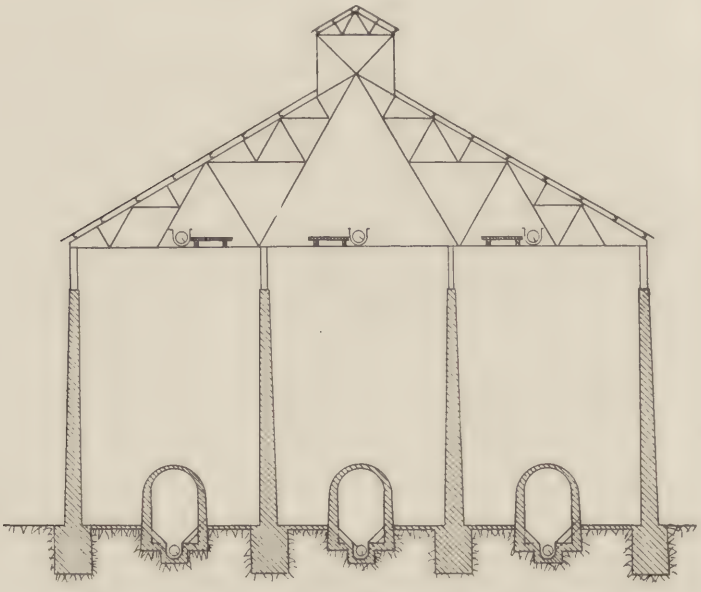


Fig. 118.—Stock house with rectangular bins and tunnels.

Silo Stock Houses.

The only type of stock house which is now built is is the silo or tank type of stock house, such as is shown in Fig. 119. Such a stock house as its name implies consists simply of a row of reinforced concrete tanks or silos. These are usually made from 25 to 40 feet in diameter and 60 to 80 feet high, each silo will then hold from 7,500 to 25,000 barrels. In addition to the circular bins there are also star-shaped bins which occur between each four tanks. In other words in a silo stock house consisting of eight silos arranged in two rows of four silos each, there will be three star-shaped bins and for each pair of tanks added there will be an additional star-shaped bin.

These stock houses are now made monolithic and with sliding forms, the concrete being poured continuously. They are usually waterproofed by adding a small percentage of hydrated lime to the concrete mixture. The silos are provided with a concrete

Fig. 119.—Silo bins and pack house, National Cement Co., Montreal, Que.

slab roof sloped only enough to secure draining off of rain water. This slab is covered with a tar and gravel or other bituminous composition roofing. The pent house on top is usually made of concrete also.

The most important feature of the design of a silo stock house, aside from the structural features are the methods of carrying the cement into and out of the bins. In the former case the use of the Fuller-Kinyon system greatly facilitates the placing of the cement into the bins. When this is not employed the cement is usually distributed by means of screw conveyors with gates in the trough.

The ports in the bottom of the bins should be so arranged and spaced that the bins will be as completely emptied as possible. Two methods are commonly employed—one (usual in stock

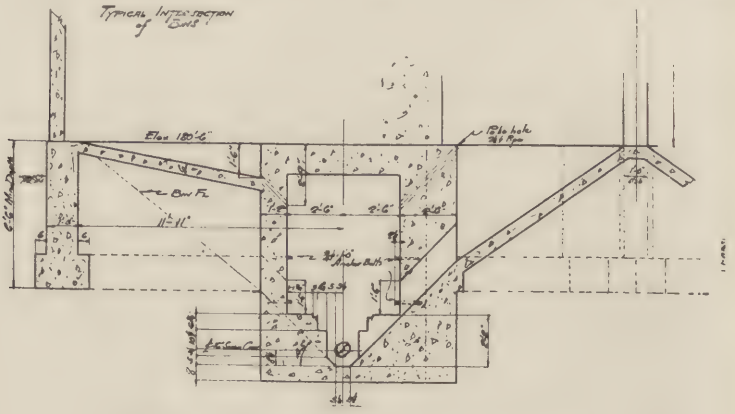


Fig. 120.—Silo stock house with sloping bottom.
Designed by Richard K. Meade & Co.

houses of the writer's design) in which a tunnel is run under the bin and the bin bottoms are sloped so as to discharge into this. (See Fig. 120). This arrangement not only allows very complete emptying of the bins, but in it the load of cement in the bins is carried directly on the ground and no heavy foundations are re-

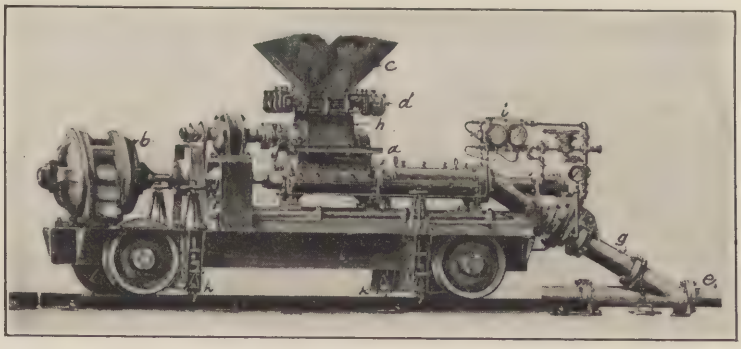


Fig. 121.—Fuller-Kinyon portable pump for emptying stock house bins—
Fuller-Lehigh Co., Fullerton, Pa.

quired. In the other system, the bottom of the bin is 6 to 8 feet above the ground level and consists of a heavy slab of reinforced concrete resting on short concrete columns and side walls. As the entire load of the contents of the bins, press on these columns they must rest on very solid and even foundation. The flat bottoms also do not allow the bins to be emptied so completely as the sloping bottom. On the other hand, this form of stock house allows ample room under the bins and working conditions here are better. The type of bin shown in Fig. 120 is the cheaper of the two.

Table XXXVIII gives the capacities of silos and interspaced bins of varying diameters.

TABLE XXXVIII.—Capacity of Silo Bins per Linear Foot of Height

Internal diameter of silo in feet	Floor area of silo in square feet	*Capacity of silo bin per foot of height in barrels of cement (376 lbs.)	Floor area of star-shaped bin between each four silos in sq. ft.	*Capacity of star-shaped bin per ft. of height in bbls. of cement
25	490.9	121.5	134	33.2
26	530.9	131.4	145	35.9
27	572.6	141.7	156	38.6
28	615.8	152.4	168	41.6
29	660.5	163.4	180	44.6
30	706.9	175.0	193	47.7
31	754.8	186.8	206	51.0
32	804.3	199.1	220	54.5
33	855.3	211.7	234	57.9
34	907.9	224.7	249	61.6
35	962.1	238.1	263	65.1
36	1017.9	252.0	278	68.8
37	1075.2	266.1	294	72.8
38	1134.1	280.7	310	76.8
39	1194.6	295.7	326	80.8
40	1256.6	311.0	343	85.0

*Weight of cement in bins 93 pounds per cubic foot or 4.04 cubic feet per barrel of cement.

Pack House.

The pack house is usually located at one end of the stock house with railroad sidings on each side. In it are located the automatic machines for packing the cement. These are usually set in a row with a belt conveyor running in front of and below them. The bags when full are dropped from the sackers on to

this belt and conveyed to the door of the railroad car. Here they discharge on to an incline table and a laborer drops them from the latter on to a truck. The sacks are usually piled four to six high on the latter. When the truck is full it is wheeled to the proper point in the car and the sacks tilted off so they remain piled one on top of the other.

Sometimes arrangements are made for taking care of and storing return bags in the pack house, but most mills now have a separate building located adjacent to the stock house for this purpose. Bags are usually sorted and counted as received and then cleaned. The cleaning may be done in a batch by a cleaning wheel. The latter consists of a wheel 8 to 10 feet in diameter by 4 to 6 feet wide made of structural steel and covered with coarse mesh wire cloth. This wheel revolves slowly in a dust-tight metal casing. The bags are placed in the wheel and as the latter revolves they tumble around and this action beats the dust out of them. Continuous cleaners which are really nothing but very light rotary inclined screens provided with tumblers and completely housed in a dustproof casing are also used. With these the bags are fed in at one end and work their way through. The clean bags fall from the lower end on to a flat belt conveyor which moves very slowly and attendants on each side of the belt pick out the torn and foreign bags as they pass by.

The only other equipment in this department consists of sewing machines for repairing bags and whatever is necessary for tying the bags. They are usually tied as received and stored in this shape in order to be ready when wanted.

Bags are usually stored in a fireproof building but, of course, the bags themselves are inflammable. In order to minimize fire risk the Security Cement & Lime Company, Hagerstown, Md., employ a compartment storage in which the bags are stored in rooms separated by fireproof partitions, each room is 18 feet by 10 feet and holds 40,000 bags. This is done in order to minimize fire by confining one should it occur to a very small part of the entire stock of bags. Ample bag storage should be provided in a modern mill since the bags come back during the winter in

northern latitudes in large quantities and are then constantly accumulating. The space required to store bags is about 45 cubic feet per 1,000 bags piled and tied. If untied and laid flat one on top the other in bales, less room is required for storage.

When two tracks are not enough for packing, small pack houses are sometimes set to one side of the main pack house and separated from each other by tracks so that a car can be loaded on each side. Two sackers are usually located in each house. The cement and bags are brought in overhead by means of a gallery connecting this auxiliary pack house with the main pack and stock house.

Packing.

Cement is packed in wooden barrels holding 380 pounds or into paper or cloth bags holding 94 pounds net by means of packers. The cement is packed as shipped and the bags or barrels are trucked directly to the cars. For this reason the packing room should be so arranged that the cars to be loaded can be brought alongside of the room and a shed roof should be run out over the cars so the loading will not be interrupted by rainy weather. Since some seasons of the year are much busier than others, the packing house should be able to load and ship at least twice as much cement as the mill can make in a day. The floor of the packing room should be on a level with the floor of the cars to be loaded. Cloth bags are used much more for packing cement than anything else. In the case of cloth bags the consumer is charged with the value of the bag, 10 cents, and credited by 10 cents when the bag is returned. The bags are all marked with the label of the brand and so each manufacturer knows his own bags. Barrels and paper bags are sold to the customer and are not returnable.

Methods employed for bagging the cement were at first of the crudest kind. Formerly machines similar to flour packers were used. The Bates valve bags and machine for filling these are now almost universally employed in America for sacking cement. The system does away with many of the defects of the

old methods of packing, including short and overweight, bags coming untied in transit, slowness of packing, need for skilled labor, etc.

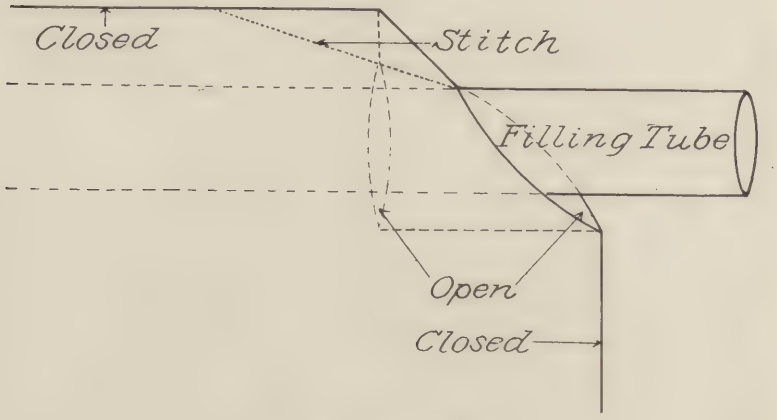


Fig. 122.—Bates valve bag.

The Bates system primarily depends upon a novel bag, of which the fundamental feature is a valve in one corner. This valve projects into the bag as is shown in Fig. 122. It is made by folding over one corner of the bag and sewing across the dotted line shown in the figure. When pressure is applied to the valve, as when the cement comes against it, the valve closes.

With this bag, the operation of filling which ordinarily consists of putting the material in the bag and then tying it, is reversed and instead, the bag is first tied and then filled, the filling being done through the valve by means of a special bagging machine which will be described a little further on. When paper sacks are used, these are closed at both ends in the bag factory, where the valve is also placed in the bag by folding and pasting. The cloth bags are tied by means of a wire tie which is twisted on to the bag by a special tool.

To fill the bag the operator has only to slip the tube of the bagging machine through the self-closing valve of the finished bag (Figs. 123 and 124). This he can do with a quick one-hand motion. A lever is then opened which permits the material to flow

into the bag. The material flows into the bag in a thin stream about one inch in diameter, and consequently there is no danger of tearing or ripping the bag. When the exact quantity of cement has been fed into the sack, the weight of the bag and contents offsets a counterpoise at the opposite end of an evenly balanced beam. The bag, of course, begins to fall and simultaneously with this,

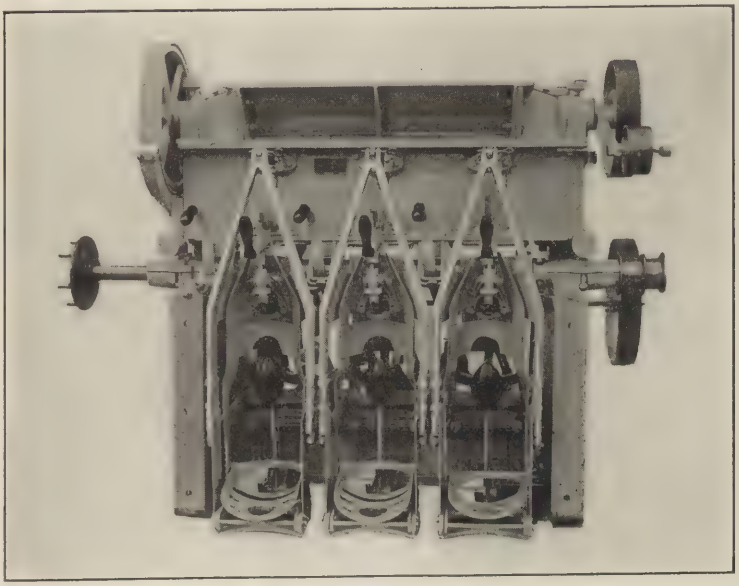


Fig. 123.—Bates valve bag packer.

the flow of material is shut off. The bag has only to move one-eighth of an inch for this to take place. It is consequently possible to make a very nice adjustment of the weight by this means.

When the bag has been filled, it is left hanging suspended by the valve spout in a position breast high to a man. From this point it is easily tilted down to the truck by means of a lever and arm.

A three-tube bagging machine will pack about 1,000 to 1,500 barrels per day of ten hours. Two men are required to operate the machine and place the bag on the trucks.

One of the greatest advantages of the valve bag is the ease with which samples may be drawn from a shipment of cement. For this purpose a small round brass tube, 1" x 18", with both ends open and one end bevelled is simply thrust into the bag through the valve of the latter and the cement which it retains

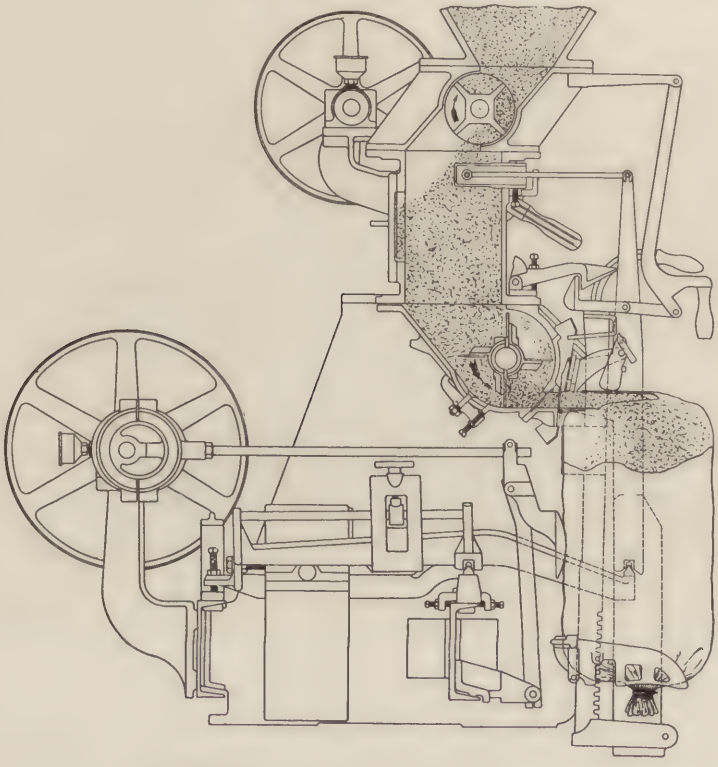


Fig. 124.—Cross section of the Bates packer, showing the course of material feeding through the machine into a valve bag.

is withdrawn for sampling. The excellency of this device and the speed with which the sampling can be done, makes it possible to sample a large number of bags in the time formerly occupied in cutting and tying one or two.

Some cement mills have a cooper shop connected with the mill. Some of these shops are equipped with barrel making machinery, and at others all the work is done by hand. At the present time, however, barrels are but seldom used except for export and water shipments. Even for the latter, double duck bags are replacing barrels and most of the cement shipped from this country for the Panama Canal was so packed.

A new development in the package line is the Bates "multi-wall" bag. This is made of five or six layers of strong water-proof paper and the joints are sewn not pasted as is usual with paper bags. This makes a strong serviceable package. These bags are of course not returnable, but as there is always a considerable loss in handling cotton sacks, the cement packed in these bags probably costs the user no more than when packed in returnable cotton bags.

CHAPTER XV

POWER EQUIPMENT, GENERAL ARRANGEMENT OF PLANT, COSTS OF MANUFACTURE, ETC.

In the early days of the industry, all of the machinery in the cement plant with the exception possibly of a few units at some distance from the rest of the plant was driven with line shafting, the latter being operated by cross-compound, condensing, engines, usually of the Corliss type. To-day, practically all American cement plants are electrically driven, the steam turbine being the most popular prime mover.

There are many points in favor of the electrical transmission of power.[1] (1) The direct connected turbine and generator is a much more efficient producer of power than the reciprocating engine. (2) The loss of power due to leakage from transmission lines is not as great as that due to friction in a long line shaft. (3) Electrical transmission allows a better arrangement of the buildings and machinery both with a view to future extensions and as regards the handling of the materials to be ground or burned. (4) Where each machine is run by a separate motor, the plant is not affected by the shutting down of any particular machine and the operation is smoother and more continuous and the speed of the driven machine more uniform. (5) Power can be purchased.

Shaft Driven Mills.

In the older mills as we have said, the machinery was usually driven by shafting. Short powerful shafts were used which were driven directly from the engine by belting or rope drives. The power was then transmitted from these shafts to the crushers and grinding mills by belts. Often the use of one or more jack shafts was necessary. Long chain and belt drives were often required to reach the elevator head shafts and the conveyors in the roofs of the building.

[1] See also "Electric Drive for Economic Operation of Cement Mills," by J. G. Porter, *Trans. A. S. M. E.*, 1914.

As a general thing, the mills grinding the raw material were operated from one engine, while those grinding clinker were driven by another. This was considered better practice than to use one large engine for both departments. It was also the general plan to run the kilns by a separate engine in order to make the operation of the latter independent of the rest of the plant and hence more continuous.

Electric Drives.

It was soon evident that certain departments of the mill could be operated better by electric motors than by a small engine, and it became the general practice, even where the raw and clinker mills were driven through shafting by powerful engines, to install an engine and generator to produce electric power and to employ motors to drive the kilns, pack house and often the crushing plant and other departments of the mill where a small amount of power was used.

One of the defects of mills actuated by horizontal pulleys, such as the Fuller-Lehigh Mill and the Griffin Mill, consisted in the necessitary of driving them by a quarter twist belt. With the introduction of the motor drive, mills of this character were driven by vertical motors.

The writer believes that the Tidewater Portland Cement Company, Union Bridge, Md., with whose construction he was connected as consulting engineer, was one of the first plants in which the individual motor drive was employed. In this plant, not only the kilns, crushers and grinding machinery were driven by individual motors, but also the conveyors, elevators, etc., were so operated. Each conveyor and elevator had its own individual motor, doing away with practically all shafting in this mill. This is now the general practice in cement plants, and in a modern mill all of the machinery, with the possible exception of the primary crusher, is driven by a direct connected motor of the proper size and speed. Usually a flexible coupling connects the motor and the machine. A magnetic coupling is often employed between the tube-mill and motor. In cases where the

machinery is very slow moving, back-geared motors are often used. A somewhat better plan, however, is to employ between the motor and the machine one of the so-called "speed reducers." These may be either of the spur-gear or of the worm-gear type.

With the development of the central station and of the hydro-electric generation of power, it has become quite common practice in the cement industry to purchase power. This is done almost universally in sections of the country where cheap hydro-electric power is available. Such a situation exists on the Pacific Coast, in the South Atlantic and Gulf States and in Canada.

At the new plants of the Universal Portland Cement Company; a subsidiary of the United States Steel Corporation, the waste gases from the blast furnaces are used to generate the power needed for the cement mill. The gas engines are located at the furnaces and are direct connected to generators. Power is transmitted some distance in each case to the cement plant.

One or two plants where oil is cheap have used engines of the Diesel type for generating power. At some of the plants in Kansas, gas engines were installed making use of natural gas for power. I believe, however, that this fuel has now become too expensive to be used by any cement plant.

Boiler Plant.

Up to about ten years ago, it was almost the universal practice in the cement industry to generate steam by hand or stoker fired-boilers and pulverized coal was never used successfully here for the generation of power, in spite of the fact that within the last few years this form of boiler firing has become very popular with large users of power. The improvement along this line in the cement industry in the last few years has consisted in the installation of the waste heat boiler which utilizes the waste heat in the kiln gases and of which more will be said later.

Practically all of the older cement plants made use of water tube boilers, generally of the horizontal type. A few plants

had vertical boilers. Probably the larger percentage of boilers were hand fired. A few plants used stokers. None used pulverized coal.

Power Required.

The actual power which will be required by any cement plant will depend to some extent on circumstances. With modern installations, however, the variation between different plants is not great. Where installations are faulty or the machinery has not been well chosen, the power required may be excessive, but the only variable which would affect the operation of a well designed plant would be the hardness of the raw materials, making more power necessary for preparing these for the kilns. As a general rule, it may be said that there will be required to operate the machinery from 1.0 to 1.5 horsepower installed for each barrel per day capacity of the mill. In other words, to operate a mill making 3,000 barrels of cement daily there will be required generators having a capacity of from 3,000 to 4,500 horsepower or 2,250 to 3,375 kilowatts.

Figured on the barrel basis, between 15 and 20 kw-hr. are required per barrel of cement produced, with an average of about 16 kw-hr. per barrel at plants properly laid out, with well chosen machinery and raw materials of average hardness. This power is proportioned about as shown below.

DISTRIBUTION OF POWER IN CEMENT MANUFACTURE UNDER AVERAGE CONDITIONS

	Kw-hr.	Per cent
Crushing and drying	1.1	6.9
Raw mill	5.8	36.2
Kiln room	0.8	5.0
Coal mill	1.0	6.2
Clinker mill	6.3	39.4
Miscellaneous	1.0	6.3
	16.0	100.0

It will be noted from the above that about 40 per cent of the power is required to crush and pulverize the raw materials, a

like amount to pulverize the clinker and the balance to operate the kilns, pulverize the coal, etc.

Waste Heat Boilers.

The attempt to utilize the heat of the kiln gases under boilers was first made, I believe, at the plant of the Nazareth Cement Company, Nazareth, Pa., in 1897 by Dr. Irving A. Bachman. Dr. Bachman placed the boiler immediately over the rear kiln housing so that the dust laden gases entered the first pass of the boiler directly after leaving the kiln. No intervening flue was employed to collect even a portion of the dust. Natural draft was used to carry the gases through the boiler. It was found impossible under these conditions to keep the boiler clean and the dust accumulated so rapidly that continuous operation of the kiln was impossible. After encountering these difficulties, the plan was abandoned and the boilers were taken away.

The late Professor R. C. Carpenter, of Cornell University, installed waste heat boilers to receive the exit gases from the rotary kilns in the plant of the Cayuga Lake Cement Company. The installation here was somewhat better than that at Nazareth, but much was still to be desired in the way of facilities for keeping the boiler clean. In this plant, one boiler of the Wickes vertical water tube type, of 3,000 square feet of heating surface was installed for each two kilns (6 feet by 60 feet) of the plant.

When these boilers were clean they gave very satisfactory results. When operated on kiln gases alone these boilers produced about 250 boiler horsepower. The same general difficulties, however, were encountered at Cayuga Lake as at Nazareth. The company, in spite of these, struggled for quite a long period to handle the dust before finally abandoning the waste heat boilers. A similar installation by Professor Carpenter at the plant of the Kosmos Portland Cement Company near Louisville, Ky., had pretty much the same history.

The efforts to use waste heat boilers were abandoned after these attempts for some years. The late Mr. Spencer B. Newberry, of the Sandusky Cement Company, however, profiting by the experiences of the early attempts, placed his boilers at a greater distance from the kiln with a substantial flue constructed between the kilns and the boilers. As the importance of this began to be realized, other engineers experimenting with the use of the waste gases for steam generation provided additional facilities for taking care of the dust and for keeping the boilers clean. It was also found advisable to employ induced draft rather than stacks.

Among the plants which installed successful waste heat boilers prior to 1915, when the subject received the almost universal attention of cement manufacturers, may be mentioned the Louisville Cement Company, the Sandusky Portland Cement Company and the Burt Portland Cement Company. With these installations about half of the steam required to operate the plant was obtained. The boilers were also generally so installed that they could be fired by hand when the kilns were not operating, or a greater quantity of steam was desired than the kiln gases could produce.

Air Leakage and Draft.

While these installations were faulty they turned the attention of the cement mill engineers to the possibilities of the waste heat boiler. It was soon realized that in the early installations due consideration had not been given to air leakage. Little or no importance was attached to the lowering of the temperature of the kiln gases by the infiltration of cold air at the feed end of the kiln. This condition occurred both in the boiler setting itself and at the opening between the kiln and the flue. In the modern installations, air seals are placed on the upper end of the kiln shell to exclude the cold air at this point. All clean-out doors on the dust chamber flues and at the bottom of each pass in the boilers are tightly fitted and in many places the joints are luted with clay which is renewed each time the doors are opened and closed. Great care is also used

in the construction of the boiler settings themselves in order to make them air-tight. In some places, the flues are housed in a steel jacket as brickwork is much more porous than steel and consequently allows air to penetrate through it.

The feature in the modern design, however, which probably did most to make the waste heat boiler practical was the increase of the intensity of and the regulation and control of the draft. It has long been known that the rate at which heat is transferred from the gas to the water in the boiler tube increases as the velocity of the gas increases, thus if the velocity of the gas should be increased three times, the heating surface could be reduced by half.

In all of the recent waste heat boiler installations, the gases have been passed through the boilers at a fairly high velocity, a draft at the exit of the boiler of from 6 to 10 inches of water being employed. It was also found advisable to lengthen the gas passages as this facilitates the transfer of heat. This was accomplished by an arrangement of baffle walls in standard boilers.

Heat in the Gases.

The amount of heat in the waste gases from the kilns depends largely on how the kilns are operated. Prior to the advent of the waste heat boiler, kilns were always operated with a view to the economical use of the fuel for burning cement. Where boilers are installed, however, kilns are often operated with a view to furnishing steam enough to operate the plant, with the result that where inefficient engines were employed the amount of coal burned per barrel of cement exceeded considerably the normal requirements for cement burning only—the manufacturer figuring that any coal lost in cement burning would be utilized in producing steam. Under normal conditions the gases leave the kiln at about 1,500° F. and there are about 12,000 cubic feet of gas per barrel of cement. The mean specific heat of the gases at the above temperature is 0.022 per cubic foot per degree rise. Assuming the tempera-

ture of the gases can be reduced to 400° F. in a proper recovery system, the heat utilized in raising steam would then be 290,400 B. t. u. The heat necessary to generate 1 pound of steam at 200 pounds per square inch gauge pressure and 100 pounds superheat from feed water at 200° F. is 1 091 B. t. u. It will be seen, therefore, that the heat in the gases is equivalent to 266 pounds of steam at the above pressure and temperature.

In a modern turbo-generator set, the requirements are about 17½ pounds of steam per kilowatt-hour at the switchboard, if so utilized, therefore, the above quantity of steam will produce 15.2 kw-hr. or practically the full requirements of a modern plant.

In actual practice, the amount of heat recovered would be reduced somewhat by the air leakage through the boiler setting and increased by the combustion in the boiler of the carbon monoxide in the gases. The kiln can always be so operated as to give a larger volume of gas and gas both of higher temperature and greater content of carbon monoxide, so that where steam turbines are employed the waste heat boilers can be made to furnish all the steam required in the plant.

By operating the kilns under reducing conditions, that is with a deficiency of air, the waste gases can be made to contain a large percentage of carbon monoxide. By admitting additional air to the gases just before or as the latter enter the boiler, the carbon monoxide is burned to carbon dioxide and the latent heat of combustion of this is added to the sensible heat in the gases. Where more steam is required for power, therefore, than would be produced by the kilns when operated normally, it is generally the practice to operate the latter so as to give a gas containing from 3 to 5 per cent carbon monoxide, the additional steam being produced by this so-called *"secondary combustion."*

Table XXXIX illustrates the performance of waste heat boiler installations at various American cement plants and also gives data as to the nature of equipment employed and operating conditions.

Quantity of Gas and Heat in This.

The heat available in the stack gases may be calculated from their temperature and analysis. It is in the case of each gas found, the product of the quantity × temperature drop × specific heat. The quantity of gas can be measured directly by means of a pitot tube or calculated from the carbon dioxide found by analysis of the gas. The latter is the simpler method and is as follows. Twelve pounds of carbon burned to carbon dioxide will unite with 32 pounds of oxygen and produce 44 pounds of carbon dioxide. Hence one pound of carbon will produce 3.67 pounds of carbon dioxide. One pound of carbon dioxide occupies 8.152 cubic feet at standard temperature and pressure. Hence 3.67 pounds will occupy 29.92 cubic feet. This is equivalent to the volume of carbon dioxide produced by the burning of one pound of carbon, therefore, one pound of coal containing 74.9 per cent carbon will produce 22.4 cubic feet of carbon dioxide. Similarly it will be found that one pound of carbon will produce 29.8 cubic feet of carbon monoxide or about the same quantity of either carbon monoxide or carbon dioxide.

From the above, it will be seen that for each pound of coal burned in the kiln there will be produced 22.4 cubic feet of carbon dioxide (or carbon monoxide). This volume of carbon dioxide is further increased by that driven off from the raw materials during burning. The amount of the latter can, of course, be determined by analysis of the raw materials and the clinker, or assumed at 200 pounds per barrel. On the latter basis, the carbon dioxide driven off from the raw materials will occupy $200 \times 8.152 = 1{,}630$ cubic feet at standard temperature and pressure. If we assume 100 pounds of coal are required to burn a barrel of cement, then the total carbon dioxide produced per barrel of cement is $1{,}630 + (22.4 \times 100) = 3{,}870$ cubic feet.

Let us assume Analysis No. 1 on page 299 as that of the gas, then it will be seen that the latter contains 27.4 per cent carbon dioxide and 0.3 per cent carbon monoxide or a combined percentage of 27.7. To find the volume of gas leaving the kilns, therefore, it is only necessary to divide 3,870 by 0.277. This gives the total volume of gas or 13,971 cubic feet per barrel of cement produced (measured at standard temperature and pressure).

To find the heat carried out by this volume of gas we could multiply the above quantity by the percentage of each gas present for the volume of gas and then the latter volume by the mean thermal capacity of the gas and temperature rise above normal. It is simpler, however, to find the mean specific heat for the mixture of gases and then multiply the total volume of gas by this and the temperature rise. For example, referring to Fig. 91, it will be seen that the mean thermal capacities of one cubic foot of air, nitrogen and oxygen are the same and since these gases (neglecting water for the present) form practically all of that portion of the gas which is not carbon dioxide, we can determine the *mean* thermal capacity of the exit gases of the kiln by multiplying the percentage of carbon dioxide by the thermal capacity of this gas and adding to this the result obtained by multiplying the difference between one and the percentage (expressed decimally) of carbon dioxide (which manifestly represents the percentage of air, oxygen and nitrogen in the exit gases) by the mean thermal capacities of the latter gases. In our case, the mean thermal capacity of carbon dioxide at 1,200° F. is found to be 0.314 and of air, nitrogen and oxygen 0.0199. The mean thermal capacity of the exit gases is, therefore, $0.274 \times 0.0314 + 0.726 \times 0.0199 = 0.02205$.

This latter is the mean thermal capacity of the gas per degree rise between 0 and 1,200° F. One cubic foot of gas at 1,200° F. will, therefore, carry out $(1{,}200 - 32) \times 0.02205 = 24.65$ B. t. u. and 13,971 cubic feet, $13{,}971 \times 24.65 = 344{,}385$ B. t. u.

In the wet process the exit gases also carry out the water evaporated from the slurry. Some water is also formed by the burning of the hydrogen in the fuel. This water is not shown by an ordinary gas analysis. The water in the slurry is, of course, 300 pounds. Coal contains, say, 4.8 per cent of hydrogen. This will, of course, produce $2 : 18 :: 0.048 : x$, $x =$ 0.432 pound of water. The quantity of coal to burn a barrel of cement will therefore produce 0.432×120 or 51.84 pounds. The total quantity of water in the exit gases is therefore $300 + 51.84 = 351.84$ or say 352 pounds per barrel of cement burned. The mean thermal capacity of steam between 212° F. and 1,200° F. is 0.54. The water, therefore, carries out $352 \times 0.54 \times (1,200 - 212) = 187,799$ B. t. u. per barrel of cement burned.

The latent heat due to carbon incompletely burned, (that is burned to carbon monoxide) is, of course, the heat which would be generated by the burning of the carbon monoxide in the kiln gases. One cubic foot of carbon monoxide burned to carbon dioxide will produce 43 B. t. u. We have previously calculated the total amount of gas at 13,971 cubic feet per barrel. This contains 0.3 per cent carbon monoxide or $13,971 \times 0.003 = 41.8$ cubic feet. The heat liberated due to combustion is of the carbon monoxide, therefore, $41.8 \times 43 = 1,787$ B. t. u. per barrel of cement.

The Boiler.

The waste heat boiler as installed at the present time consists of a standard horizontal water tube boiler. Fig. 125 shows the method of installing the boiler and of making the connection with the kiln, etc. In a dry process cement plant where the gases are at approximately 1,500° F., ten square feet of heating surface are employed for each boiler horsepower. Sometimes the boilers are equipped with superheaters. Originally one boiler was employed for each kiln. This is considered disadvantageous, however, and now only a few large boilers are employed even where there are quite a number of kilns. By having fewer and larger boilers efficiency is increased and floor

space is decreased. The number of openings permitting air leakage is also cut down and there are fewer units to look after and clean. The boilers should be set fairly close to the kiln. There should, however, be installed between the boilers and the kiln a

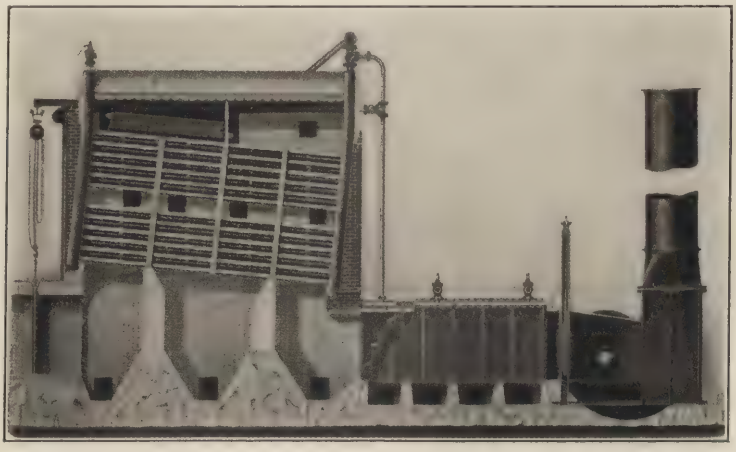


Fig. 125.—Waste heat boiler installation—Edge Moor Iron Co., Edge Moor, Del.

large flue in order that some of the dust may settle. This flue is usually provided with a hopper bottom and openings through which the dust may be drawn into a conveyor located alongside of the flue.

Boilers are usually provided with four passes. The tubes are usually kept clean by blowing them off at least once a day with a steam or air jet. Openings are provided for this purpose in the sides of the boiler.

Air Seal and Dampers.

The waste heat boiler owing to its recent adaptation to the cement industry has generally been installed in plants which have been previously designed for hand fired boilers and for kilns which were intended to discharge their gases directly into the atmosphere through individual steel stacks. These stacks have generally been left in place and the only change

which has been made in the kiln itself is to provide an air seal between the kiln and the stack housing.

Fig. 126 shows a form of seal which has been quite generally used in the cement industry. It will be noted that this consists of a plate "A" rivetted to the kiln. There is keyed to this plate a cast iron ring "B." This is free to move hori-

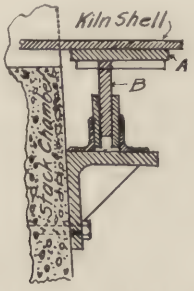


Fig. 126.—Air seal for feed end of kiln.

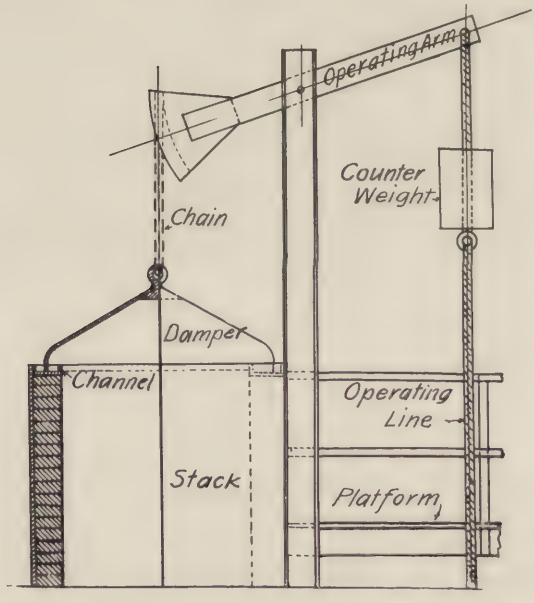


Fig. 127.—Damper for kiln stacks, waste heat boiler installation.

zontally up and down on the kiln but is caused to revolve with the kiln by the keys. Any expansion or contraction in the kiln is taken care of by the sliding of the ring over the plate. This ring in turn revolves in a close fitting groove made by two angle irons which are fastened to a round box arrangement on the stack chamber.

The kiln stack is generally provided with a damper. This should effectively close the stack so that no cold air can leak in at this point. Fig. 127 shows an acceptable form of damper. Still another damper is usually placed between the kiln and the boiler so that when the kiln is not in operation the port connecting the kiln with the boiler can be closed. It is advisable to make the outer casing of the flue either of reinforced concrete or of steel.

The steel jacket as has been previously noted is impervious to air, particularly if the joints in this flue are welded instead of riveted. From the main flue the gas is distributed to the boilers through short connecting flues. The boilers themselves are usually set quite high so as to allow a large chamber underneath the tubes in which the dust may settle. Clean-out doors are provided at the bottom of this space so that dust can be removed at intervals.

Economizer, Fan, Etc.

The boilers are now quite generally followed by economizers in which the feed water for the boiler is heated. The gases leave the boiler at a temperature of from 475 to 600° and they are further reduced in the economizer to about 300 to 350° F. The economizer is set immediately after the boiler and is followed by the draft fan.

Owing to their higher velocities, economizers on waste heat boilers have a greater capacity than in ordinary power plant work and should have about 33⅓ per cent of the heating surface of the boiler to which they are connected. Economizers should have steel plate sides packed with asbestos or other heat insulator to conserve heat, cut down air leakage, etc. An

TABLE XXXIX.—Data on Waste Heat Boiler Operation

Plant	A	B	C	E	F	G
Process	Dry	Dry	Dry	Wet	Dry	Dry
Type of boiler	Edgemoor	B. & W.	Sterling	Edgemoor	Edgemoor	Edgemoor
Number of boilers	2	2	7	2	3	2
Number and size of kilns connected to boiler	6–7x100	2–10x150 2–7x100 2–8x125	7–8x100	2–10x150	6–6½x100	5–8x125
Clinker per hour—bbls.	115	150	107	87.7	112	140
Square ft. heating surface each boiler	7,493	15,300	3,450	6,384	7,493	10,662
Square ft. heating surface superheater	747	691	None	—	400	—
Economizer heating surface, sq. ft.	2,010	None	None	2,142	2,010	2,300
Draft at feed end of kiln, ins. water	0.3	0.25	0.07	0.12	0.45	0.40
Draft at fan inlet, ins. water	3.9	5.00	No fan	4.30	6.80	4.50
Temperature of gas leaving kiln ° F.	1,450	1,300	1,350	1,100	1,300	1,300
Temperature of gas leaving boiler or economizer ° F.	336	430	600	390	436	310
Fuel—kind	Bit. coal	Bit. coal	Bit. coal	Bit. coal	Bit. coal	Oil
Fuel—heating value, B. t. u. per lb., B. t. u.	13,000	13,000	13,000	12,780	13,500	19,000
Coal required per barrel of clinker	89.09	103	109	127.2	95	8.90 gal.
Carbon dioxide in gas leaving kiln	28.8	20.5	24.1	27.5	26.5	24.0
Carbon dioxide in gas leaving fan	14.9	18.0	—	18.7	14.0	—
Steam produced under operating conditions, lbs. per hour	25,744	53,760	25,320	35,000	70,113	70,000
Steam produced under operating conditions, lbs. per barrel	310	391	340	411	457	500
Steam produced under operating conditions, lbs. per lb. of coal burned	3.48	3.80	3.12	3.22	4.81	—
Boiler horsepower developed	833	1,680	1,350	1,160	2,030	2,230
Steam pressure of boilers—lbs. per sq. in.	158	155	150	175	170	185
Temperature of steam at boilers, ° F.	430	430	366	510	390	480

efficient economizer will show a saving of from 8 to 10 per cent. The draft fan should be a heavy duty fan. The bearings are made extra large and are generally water cooled. The blades are so shaped that dust will not accumulate on them. The wheel and rotor are made heavy so that accumulation of dust will not affect smooth running.

A draft at the fan inlet of from 6 to 8 inches of water is usually employed. With 6-inch draft the loss of pressure is about as follows:

	Ins.
In the kiln	0.5
In the flues	0.5
In the boiler	4.0
In the economizer	1.0

The fans are driven by either small steam turbines or by electrical motors. The motors are generally considered the better arrangement as they operate independently of the steam pressure in the boiler. With the turbine, when the steam pressure in the boiler is low, the speed of the turbine, and consequently the speed of the fan is reduced correspondingly and this happens to be the very time that full draft is needed. The motor on the other hand is independent of conditions in the boiler.

When the temperature of the available feed water is low it is more economical to employ turbines and exhaust these to a feed water heater, but when the feed water can be heated to a temperature of about 200° F. by other equipment, the electric motor is preferable.

Auxiliary Departments

The auxiliary departments of the cement plant consist of a building or buildings in which are housed the mill office, laboratory, machine-shop, store-house, electrician's shop, carpenter's shop, blacksmith's shop, oil supply, lavatories and wash room, first-aid station and dispensary, etc.; and where electrical power is purchased, a transformer-house. Often, all of these departments are housed in one long building, but gener-

ally two or more buildings are employed particularly if the plant is large. The mill office and laboratory are quite often housed in the same building and if much clerical work is done at the mill this should not be too near the plant on account of the dust. The various shops are generally housed in one building and this often contains the store-house also. Oil and grease are usually stored in a separate building. The shops are best located convenient to the grinding mills as these need repairing most.

The equipment of the laboratories is quite fully discussed in the next chapters of this book. The space necessary depends entirely on the size of the plant. The chemical laboratory for a 3,000-barrel plant will require about 400 to 600 square feet which should be divided into at least two rooms, a large laboratory proper and a small office and balance-room combined. The physical laboratory may consist of one large room of about 350 square feet. There should also be a small room or a large closet connected with the laboratories for supplies.

The mill office will depend entirely on what clerical work is done at the mill. When this is limited to keeping account of pay-rolls, supplies, mill correspondence, cost of manufacture, etc., one large general office and a smaller one for the mill superintendent will answer. If the purchasing agent is located at the mill he should, of course, have his own office.

Most mills now have a room set aside for a first-aid station. This is equipped with the appliances and supplies ordinarily found in the offices of a physician and is usually furnished and stocked under the advice of the latter. The inside of this room should be painted white and the floor be of tile or hard wood. Where dispensary service for the employes is maintained two small rooms are generally found advisable—one for a waiting room and one for a consulting room.

Machine-Shop.

The machine-shop should, where possible, be located adjacent to the grinding departments of the mill as the heaviest repairs

are connected with these. Even the smallest cement mill will need a fairly well equipped shop. The equipment of this will include such tools as a small and a large lathe, drill-press, planer, shaper, milling-machine, hack-saw, pipe and bolt-threader, emery-wheel, grindstone and acetylene outfit. There will, of course, be benches and a full supply of bench tools.

It is advisable to place a small hand operated overhead traveling crane in the machine shop and also a track on which to bring in parts should run lengthwise through the shop. Where the crane is not employed an I-beam and overhead trolley block should be installed.

The blacksmith's shop should have a forge, an anvil and the usual forge tools. Often a small trip-hammer is installed and mechanical tools for sharpening and shaping rock-drills are very useful and pay for themselves very soon. The blacksmith's shop is often housed in one end of the machine shop. When the quarry is at some distance from the mill another shop is placed here for taking care of the sharpening, etc., of the drills.

The store-house is, as its name indicates, the room in which the repair parts and mill supplies, except gypsum and oil, are kept. It consists simply of a large room provided with racks and bins for the smaller parts, the larger parts being kept on the floor.

The electrician's shop is usually adjacent to the machine shop or store-house. Here are kept a few spare motors and motor parts and here repairs to motors are made. The electrician is generally provided with a full set of test instruments, etc. Lamps and other electrical supplies are often kept here rather than in the store-house.

All repair parts, supplies and machine shop labor expended in making repairs are kept account of and are charged against the department in which the latter occur.

Where power is purchased, a transformer-house has to be provided. In this are housed the transformers and the switchboard. The transformer building should be located as near the grinding

mills and crushing department as possible since approximately two-thirds of the power is used here.

The oil house is provided with tanks, filters, etc., and should be near enough to the store-house to allow one man to attend to both but separated from it in order to lessen fire danger.

Arrangement of Plant.

Before the advent of the individual motor drive it was necessary to so arrange the mill as to best distribute the power. Now when electric drives are employed, the various departments of the mill may be grouped in almost any desired manner. The general idea now among cement engineers is to so arrange the mill as to facilitate elevating and conveying of the materials. Following out this idea, the various departments are usually grouped so that the materials move naturally from one step to

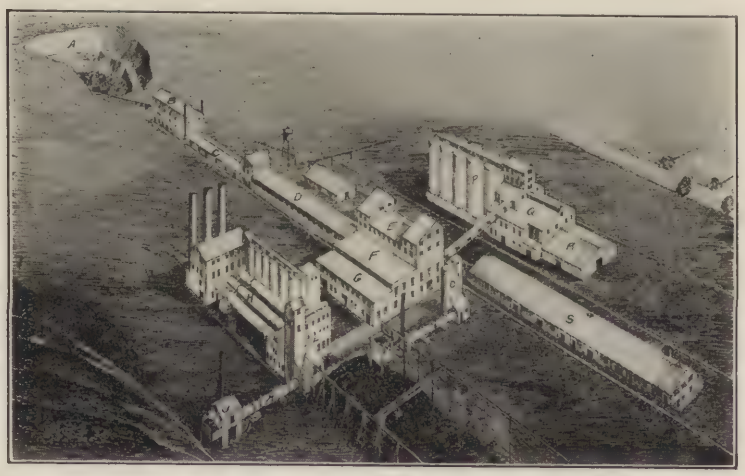


Fig. 128.—Bird's-eye view National Cement Co., Montreal, Que., Richard K. Meade & Co., Engineers.

Explanation: *A*, Quarry; *B*, Crushing plant; *C*, Rock dryers; *D*, Rock storage; *E*, Bradley-Hercules mill room; *F*, Tube-mill room; *G*, Synchronous motor room; *H*, Blending silos and kilns; *L*, Coal pulverizing room (Aero pulverizers); *K*, Coal dryer; *J*, Coal crushers and unloading department; *M*, Clinker Storage; *N*, Clinker dryer; *O*, Gypsum storage; *P*, Cement storage; *Q*, Pack-house; *R*, Bag storage; *S*, Machine-shop, stores, office, laboratory, etc.

the next. The relation of the railroad sidings and quarries also has an important bearing on the arrangement of the mill. The use of the Fuller-Kinyon pump, however, allows the coal mill and the stock house to be placed at almost any desired angle to and at some distance from the rest of the plant and hence allows more flexibility in the layout.

Figs. 128 and 129 give an idea as to the layout of a modern cement plant. The former illustrates the arrangement of the tracks and equipment in a dry process plant while the latter shows a wet process plant.

Table XL gives the equipment employed in a number of American Portland cement plants. This information is taken from published descriptions of these plants and may not represent present conditions exactly at any plant. The descriptions, however, show quite clearly what equipment is necessary for plants of the size indicated and taken in connection with the preceding chapters should enable the reader to form a good idea of a modern cement plant.

TABLE XL.—MECHANICAL EQUIPMENT OF SOME MODERN PORTLAND CEMENT PLANTS.

Allentown Portland Cement Co.

Materials—Cement-rock and limestone. Dry process. Fuel—coal.
Capacity—2,800 barrels daily. Location—Evansville, Pa.

Quarry Equipment.

Deep well drilling machine.
End dump cars, capacity 75 cubic feet.
1 Marion shovel—65 tons.
1 Atlantic shovel—65 tons.
1 Thew shovel for stripping.
Electric hoists, incline and automatic car dumping arrangement.

Stone House.

1 No. 10 McCully crusher.
3 No. 6½ Lehigh crushers.
1 Motor, 250 H. P. used to drive crushers.
4 Waste heat dryers, 7′ × 50′.
1 Motor, 50 H. P. for driving all above.
Stone storage, capacity 5,000 tons.
1 Volume mixing apparatus.

Raw Mill.

2 No. 8 Krupp ball mills, without screens, each driven by a 50 H. P. motor.

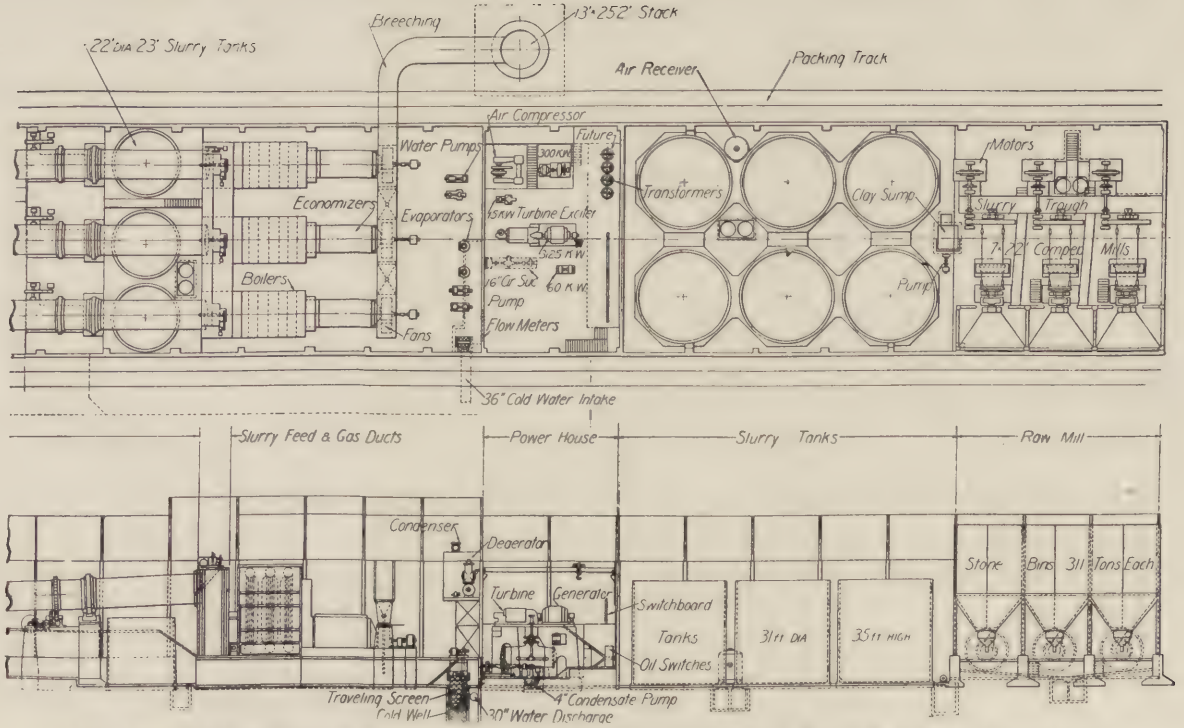


Fig. 129-a.—Plan and elevation—Manitowoc Portland Cement Co., Manitowoc, Wis., raw mill, slurry tanks, power house, waste heat boilers, and feed end of kilns.

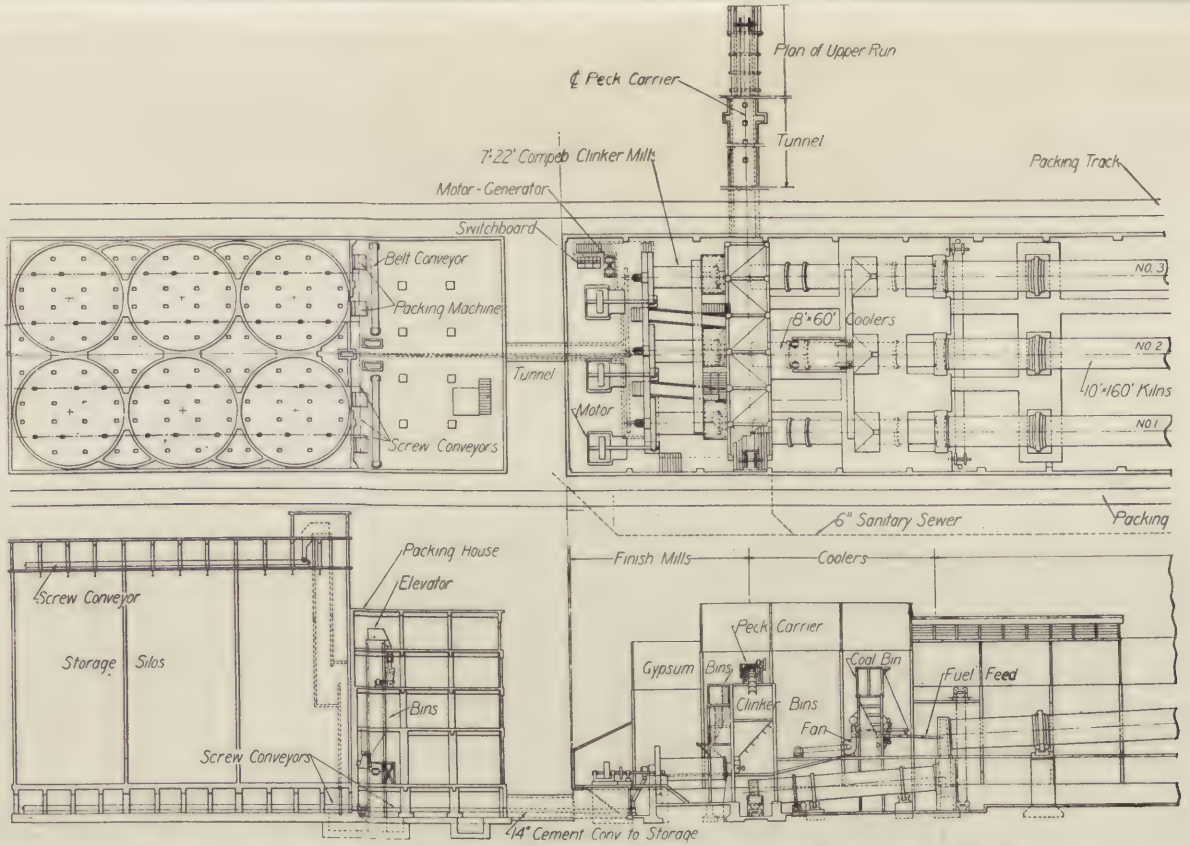


Fig. 129-b.—Plan and elevation—Manitowoc Portland Cement Co., Manitowoc, Wis., discharge end of kilns, coolers, finishing mill, stock house, and pack house.

11 Fuller-Lehigh mills, 42″, each driven by a 75 H. P. vertical motor.

Kiln Room.

4 Rotary kilns (Wetherill), 8′ × 120′, each driven by a 30 H. P. variable speed motor.

4 Rotary coolers, 5′ × 50′, all driven from a line shaft by one 50 H. P. motor.

Clinker storage consisting of steel trestle above and tunnel below, with belts for conveying. Capacity 90,000 barrels.

Finishing Mill.

1 No. 8 Krupp ball mill, without screens, driven by 50 H. P. motor.

5 Fuller-Lehigh mills, 42″, each driven by a 75 H. P. vertical motor.

3 Fuller mills, 54″, driven by individual vertical motors.

2 Fuller mills, 57″, driven by individual vertical motors.

Stock house with a capacity of 120,000 barrels.

4 Bates automatic valve bag packers.

Fuel Mill.

1 Set rolls, driven by 40 H. P. motor.

2 Matcham coal dryers, driven by 30 H. P. motor.

3 Fuller-Lehigh mills, 42″, 75 H. P. motor for each.

Fuller-Kinyon System for handling pulverized coal.

Coal storage for handling coal as unloaded.

Power Plant.

3 Wetherill cross-compound condensing engines, direct connected to (Westinghouse) A-C. generators, 937 kv-a. each.

1 Relay unit.

1 Motor generator set for exciting.

1 Engine-driven generator for exciting.

5 Rust vertical tubular boilers, 40 H. P. each.

5 Sets Lehigh stokers.

1 Traveling crane, 10 tons.

Mesta barometric condenser, pumps, etc.

All machinery is motor-driven and most of it by individual motors Buildings are of steel and plastered expanded metal.

Dixie Portland Cement Co.[1]

Materials—Limestone and shale. Wet process. Fuel—coal. Capacity—6,000 barrels daily. Location—Copenhagen, Tenn.

Quarry Equipment.

4 Well drilling machines.

3 Porter steam locomotives.

Steam shovels for loadng.

Side dump all steel quarry cars.

Electric hoisting engine.

[1] *Rock Products*, Oct. 10, 1924, 27.

Belt conveyor (2,200 feet) from shale pit to mill.

Stone House.

1 No. 42 McCully crusher, driven by its own electric motor (for limestone), followed by,

1 Revolving screen, 2″ openings, followed by

1 Worthington 72″ diam. × 30″ face rolls.

Raw material storage, 80′ × 240′, equipped with Shepard traveling crane, capacity 30,000 tons.

4 Williams hammer mills (for shale).

2 Shale storage tanks, capacity 300 tons each.

Raw Mill.

2 No. 106 Smidth kominuters, driven by 300 H. P. motors, followed by,

2 Smidth Trix screens followed by,

2 Smidth 7′ × 27′ tube mills, driven by 500 H. P. motors.

1 Blending tank, 3,200 barrels capacity.

8 Slurry storage tanks, 900 barrels capacity each.

Kiln Room.

10 Rotary kilns, 8′ × 125′, each driven by a 30 H. P. motor.

5 Revolving coolers.

Finishing Mill.

20 Griffin mills, 30″.

2 Tube mills, 7′ × 27′.

Stock house with a capacity of 300,000 barrels.

7 Automatic weighing and sacking machines.

Fuel Mill.

1 Coal crusher.

2 Rotary coal dryers.

5 Fuller-Lehigh mills, 42″.

Power Plant.

There are two power plants, one driving the raw mill and one for the clinker mill, in each of which are

1 Direct-current generator, 400 kw.

3 B. & W. water tube boilers, 700 H. P. each.

3 Westinghouse turbo generators, 1,200 kw. each.

1 Reinforced concrete chimney, 150 feet high.

Buildings are of reinforced concrete or of steel and plastered expanded metal. Roofs are of corrugated iron.

This represents a mill built some years ago and rebuilt and enlarged recently.

Security Cement & Lime Co.[1]

Materials—limestone-shale and boiler ashes (cinders). Dry process. Fuel—coal.

Capacity—5,000 barrels daily. Location—Security, Md.

[1] *Concrete*, August, 1923, p. 21, *Cement Mill Edition.*
Rock Products, Nov. 15, 1924, p. 35.

Quarry Equipment (located one-fourth mile from mill).

2 Sanderson cyclone steam well drills.
1 Loomis clipper electric well drill.
1 Marion steam shovel, Model 70, 4-cubic yard dipper
1 Marion steam shovel, Model 65, 2½-cubic yard dipper.
1 Marion electric shovel, Model 70, crawler tread.
1 Thew traction steam shovel, A-1, ¾-cubic yard dipper.
1 Vulcan saddle tank locomotive, 26 tons.
Side dump, 10 ton, quarry cars.

Crushing Plant (located at quarry).

1 Flory 48″ drum electric hoist for hauling up incline.
1 Mundy hoist for dumping.
1 Allis-Chalmers 54″ × 60″ jaw crusher driven by 200 H. P. motor.
1 Allis-Chalmers screen 60″ × 25′, for commercial stone.
2 McCully gyratory crushers, No. 7½.
Raw Material storage, concrete, 50′ wide × 230′ long × 35″ high, capacity 12,000 tons. Material delivered in and out of storage by belt conveyors.
1 Steel loading hopper, 100 tons capacity.
Stone transported to mill by 50-ton standard gauge hoppered car.
1 Vulcan locomotive, 26 tons.

Raw Mill.

1 Receiving hopper, 125 tons capacity.
3 Crushed stone tanks, capacity 927 tons combined.
1 Pennsylvania hammer mill, size SXP-8, for stone.
1 Jeffrey hammer mill, Type B, for cinders.
3 Vulcan dryers, 5′6″ × 50′.
2 Storage tanks, 1,300 tons capacity combined.
1 Schaffer poidometer.
17 Fuller-Lehigh mills. (8 mills are driven by two 300 H. P. synchronous speed motors through line shafting; 5 mills are driven by 75 H. P. individual vertical motors; 4 mills driven in pairs by two 150 H. P. motors).

Kiln Department.

5 Rotary kilns, 10′ to 8′ × 125′.
Clinker storage, 55,000 barrels capacity, equipped with Niles crane.

Fuel Mill.

1 Cummer dryer, 48″ × 36′.
3 Fuller-Lehigh mills, 42″, driven by individual 75 H. P. vertical motors.

Finishing Mill.

10 Giant Griffin mills.

4 Krupp tube mills. 6′ × 16′.

(Two 300 H. P. synchronous motors each drive 5 Griffin mills and one tube mill through line shafting; 5 Griffin mills are driven by individual 75 H. P. vertical motors; and 2 tube mills have 250 H. P. individual motors).

Stock House.

8 Reinforced concrete silos, 30′ diameter × 70′ high, capacity 100,000 barrels.

1 Wooden stock house, 100,000 barrels, capacity.

5 Bates packers.

Power purchased.

This represents a mill built some fifteen years ago and greatly enlarged and remodeled in recent years.

National Cement Co.

Material—cement rock. Dry process. Fuel—coal.

Capacity—3,300 barrels daily. Location—Montreal-East, Quebec, Canada.

Crushing Department.

1 Flory single-drum car hoist, 54″ × 36″, operated by 350 H. P. motor.

1 Pennsylvania single-roll crusher, class M, 36″ × 60″, driven by 200 H. P. motor.

1 Pennsylvania hammer mill, Super G-12, direct connected to 300 H. P. motor.

1 Overhead traveling hoist, 10 ton.

2 Dryers, 6′ × 70′, each driven by 15 H. P. motor.

1 Aero pulverizer for coal for heating dryers, D-1, driven by 40 H. P. motor.

Stone storage, 44′ × 150′. Capacity 6,000 tons.

Material handled in and out by belt conveyors.

Raw and Clinker Mill.

4 Bradley-Hercules mills, direct connected to 300 H. P. motors.

4 Canadian-Vickers tube mills, 7′ × 26′, direct connected to G. E. super-synchronous, 500 H. P. motors

Any unit can be employed for either raw material or clinker.

Fuller-Kinyon System used for handling ground raw material and cement.

Kiln Department.

6 Reinforced concrete blending silos, 15′ diameter × 43′ high.

3 Vulcan kilns, 9′ × 160′, each driven by 50 H. P. motor.

3 Aero pulverizers, G-1, direct connected to 100 H. P. motors.

1 Spare aero pulverizer as above mounted on truck.

1 Coal dryer, 6′ × 60′, driven by 15 H. P. motor.
1 Pennsylvania single-roll coal crusher, 24″ × 24″ driven by 25 H. P. motor.
Drag line scraper for handling coal in and out of storage.
No coolers.
Clinker storage, 100′ × 250′, capacity 200,000 barrels clinker, equipped with Shepherd 5-ton crane and 2-yard basket.
1 Clinker dryer, 6′ × 70′. Wet seasoned clinker to be dried by mixing with hot fresh clinker.
1 Gypsum silo, 15′ diameter × 52′ high.

Stock House.

10 Reinforced concrete silos 30′ diameter × 65′ high, 126,000 barrels capacity.
3 Bates packers direct connected to 15 H. P. motors.

Power is purchased but provision has been made for waste heat boiler plant if desired. Large motors employ 2,200 volts, small motors 550 volts. Buildings are of structural steel.

Pyramid Portland Cement Co.[1]

Materials—limestone and clay. Wet process. Fuel—coal.
Capacity—2,500 barrels daily. Location—Valley Junction, Iowa.

Quarry Equipment—Quarry located at Gilmore City, 100 miles from mill.
2 Cyclone well drills.
1 Bucyrus steam shovel, 100 tons, 3½-cubic yard dipper.
Standard gondola cars for transporting stone to mill.

Crushing Plant (at mill).

1 Clyde double-drum electric car hoist.
1 Chicago rotary car dumper, operated by 10 H. P. motor.
1 McCully gyratory crusher, No. 18.
1 Dixie hammer mill, No. 9, (crusher and mill driven by 300 H. P. motor).
1 Revolving stone screen, 5′ × 30′ (this is used to produce commercial stone of which plant sells some).
1 Raw material, gypsum, coal and clinker storage, 78′ wide × 400′ long, equipped with Milwaukee 8-ton traveling crane with 3-yard clam shell bucket. Capacity of storage 15,000 tons of stone, 5,000 tons shale and 100,000 barrels clinker. Material reclaimed on belt conveyor.

Raw Mill.

2 Kominuters, driven by 150 H. P. motors.
2 Trix screens, driven by 10 H. P. motors.
2 Smidth tube mills, 7′ × 22′, driven by 400 H. P. motor through Lenix drive.

[1] *Rock Products*, October 20, 1923, p. 45.

3 Correcting basins, 600 barrels capacity each, agitators driven by 5 H. P. motors.

1 Mixing basin, 2,000 barrels capacity, mechanical agitators driven by 15 H. P. motor.

3 Smidth plunger pumps for handling slurry.

Kiln Department.

3 Kiln feed basins, capacity 2,700 barrels, mechanical agitators driven by 15 H. P. motors.

2 Rotary kilns, 11′ 3″ to 10′ × 240′, reinforced concrete stacks 216′ high.

2 Rotary coolers, 7′ × 70′ equipped with fans.

Clinker storage as noted.

Fuel Mill.

1 Dixie crusher.

1 Cummer coal dryer, 6′ × 50′.

3 Raymond roller mills.

Finishing Mill.

3 Kominuters.

2 Smidth tube mills, 7′ × 22′.

Stock House.

6 Reinforced concrete silos, 32′ diameter × 80′ high, capacity 110,000 barrels.

2 Bates packers.

Power is purchased.

Signal Mountain Portland Cement Co.[1] 1922

Materials—Limestone and clay. Wet process. Fuel—coal.

Capacity—2,500 barrels daily. Location—Signal Mountain, Tenn.

Quarry Equipment (Quarry located one-third mile west of plant).

2 Sanderson cyclone well drills, No. 14.

1 Air compressor driven by 125 H. P. motor.

1 Bucyrus steam shovel, No. 85-C, 3½-yard dipper.

10 Western side dump, air operated cars, 16 yards capacity.

1 Baldwin locomotive, 50 tons.

Crushing Department.

1 Allis-Chalmers gyratory crusher, No. 21, driven by 200 H. P. motor.

2 Williams Hammer mills, No. W-2, driven by 150 H. P. motors.

Storage 80′ × 350′ capacity, 15,000 tons of stone and 5,000 tons of clay equipped with traveling crane.

Raw Mill.

1 Wash-mill for clay, 26′ diameter; agitator driven by 75 H. P. motor.

2 Allis-Chalmers compeb mills, 7′ × 22′, driven by 500 H. P. syn-

[1] *Concrete*, January, 1924, p. 1, *Cement Mill Edition.*

chronous motor through magnetic clutch.
4 Steel blending tanks, each 290 yards capacity, air agitation.
1 Air compressor, driven by 100 H. P. motor.
3 Centrifugal pumps, rubber-lined, 4″, driven by 40 H. P. motors.

Kiln Department.

2 Kiln feed tanks, each 600 cubic yards capacity, air agitation.
2 Rotary kilns, 11′ × 175′, each driven by 75 H. P. variable speed motor.
2 A. B. C fans, No. 9, each driven by 25 H. P. motor.

Fuel Mill.

1 Webster single roll crusher, 30″ × 30″.
1 Rotary dryer, 8′ × 55′.
2 Fuller mills, 46″, driven by 100 H. P. motors.
Coal conveyed to kilns by Fuller-Kinyon system.

Finishing Mill.

2 Allis-Chalmers compeb mills, 7′ × 26′, driven as above.

Stock House.

6 Reinforced concrete silos, 35′ diameter × 85′ high, capacity 90,000 barrels.
2 Bates packers.

Buildings are of structural steel, with concrete floors and concrete roof tile.

Electrical power is purchased but provision has been made for a waste heat boiler plant at any time.

Oklahoma Cement Co.[1]

Raw Materials—Limestone and shale. Wet process. Fuel—natural gas. Capacity—4,500 barrels daily. Location—Ada, Okla.

Quarry Equipment—Quarry located about six miles from mill.

Keystone well drills.
2 Marion steam shovels, No. 80, 3-yard dipper.
10 Woodfort Engineering Company electric-driven, 10-ton side dump cars, each operated by 35 H. P. motors—switches are controlled from crusher building.

Shale Pit.

2 Steam shovels, No. 60-E, 2½-yard dippers.
Side dump gondola cars are used for shale.

Crushing Plant.

1 Traylor jaw crusher, 36″ × 72″.
1 Scalping screen, 64″ × 18′6″.
1 Mammoth Jumbo Williams mill, No. 9.

[1] *Concrete*, September, 1920, *Cement Mill Edition.*

2 Double-jacketed revolving screens, 84″ × 26′.

(About 1,500 tons of stone is sold daily.

Stone House.

Material delivered to plant by rail.

Stone storage, 80′ wide × 300′ long × 70′ high, half for each material. Materials enter by overhead tracks. Material reclaimed by 15-ton, 4-cubic yard crane.

One 20′ bay in middle used as proportioning department, Schaffer poidometers used for proportioning.

1 Double roll shale disintegrator, 36″ × 36″.

Raw Mill.

3 Allis-Chalmers compeb mills, 7′ × 26′, driven by 450 H. P. synchronous motors through 54″ magnetic clutch.

3 Correcting basins, each 20′ diameter × 14′ high, Dorr agitators.

2 Mixing basins, each 34′ diameter × 14′, Dorr agitators.

2 Slurry storage basins, 34′ diameter × 22′ high, Dorr agitators.

Kiln Room.

3 Four-tire, rotary kilns, 10′ × 240′, equipped with concrete, stacks 9′ × 270′, driven by 100 H. P. variable speed motors.

3 Fans, capacity 9,000 cubic feet minimum at 6-ounce pressure.

Natural gas used as fuel—two 17″ Kirkwood burners for each kiln.

3 Rotary coolers, 8′ × 80′.

10 Reinforced concrete silos, 26′ diameter × 85′ high, for clinker storage, capacity 135,000 barrels.

Finishing Mill.

3 Compeb mills, 7′ × 26′, driven as above.

3 Emerick separators, 14′ diameter.

Stock House.

10 Reinforced concrete silos, 26′ × 85′ capacity, 125,000 barrels.

4 Bates packers.

Power is purchased, 480 volts is employed in mill. Buildings are of reinforced concrete.

Petoskey Portland Cement Co.

Materials—Limestone and shale. Wet process. Fuel—coal.

Capacity—2,000 barrels daily. Location—Petoskey, Mich.

Quarry Equipment.

Well Drills.

1 Steam shovel, 70 tons for limestone.

1 Steam shovel, 45 tons for stripping.

Side dump cars, 10 tons.

Steam locomotive.

Stone House.

1 Gyratory crusher, No. 12.
4 Rotary screens, 5′ × 14′.
3 Gyratory crushers, No. 5.
(About 1,000 tons of stone are sold daily for commercial purposes).

Raw Mill.

2 Allis-Chalmers compeb mills, 7′ × 22′, each driven by 400 H. P. synchronous motors through magnetic clutches.
4 Slurry tanks, each 20′ diameter × 40′ high, air agitation.
Slurry handled by compressed air and blow tank.

Kiln Room.

2 Allis-Chalmers kilns, 10′ × 150′.
2 Kiln feed tanks, 20′ × 20′.
2 Coolers, 6′ × 60′.
No clinker storage. Clinker conveyed direct to mills by Peck carrier.

Fuel Mill.

1 Indirect fired coal dryer, 6′ × 60′.
3 Fuller mills, 42″.
Coal conveyed by elevator and conveyors.

Finishing Mill.

2 Compeb mills, 7′ × 22′, driven as noted above.

Stock House.

6 Reinforced concrete silos, 30′ diameter × 70′ high, capacity about 100,000 barrels.
Bates valve baggers.

Power Plant.

2 Edgemoor boilers, four-pass, 638 H. P., equipped with superheater, waste heat.
2 Green economizers.
2 Buffalo exhausters, 580 R. P. M., driven by 75 H. P., variable speed motors.
1 Boiler, 313 H. P., spare.
2 Allis-Chalmers turbo-generators, 1,000 kv-a. each.
2 Jet condensers.
1 Exciter set, steam-driven, 30 kw.
1 Exciter set, motor-driven, 30 kw.
2 Air compressors, motor-driven, capacity each 300 cubic feet minimum.
Large motors employ 2,300 volt, 60-cycle, 3-phase current, small motors 480 volts.
Crusher building is of reinforced concrete, balance of plant of steel.

International Cement Co., Birmingham Plant[1]

Materials—Limestone and shale. Dry process. Fuel—coal.
Capacity—4,700 barrels daily. Location—North Birmingham, Ala.

Quarry Equipment.

2 Cyclone electric well drills.
Eastern Car Company V-shaped, 10-ton side dump cars.
2 Marion, Model 37, electric shovels, full revolving, caterpillar tread.
1 General Electric storage battery locomotive, 8-ton.
1 Devenport steam locomotive, 15-ton.
1 Single drum Flory hoist, driven by 100 H. P. motor.
1 Single drum hoist for dumping cars, driven by 15 H. P. motor.

Stone House.

1 Superior gyratory crusher, 30″ driven by 150 H. P. motor.
1 Pennsylvania hammer mill, Model Ajax, No. 8, driven by 200 H. P. motor.
Stone storage, 82′ wide × 195′ long, with one large bin for stone and three small bins for shale. Material handled by Champion, 8-ton, crane and 3-yard Blaw-Knox clam shell bucket.
2 Bins, 15′ × 15′ × 15′, one each for stone and shale, equipped with Schaffer poidometers for proportioning these.
2 Vulcan rotary dryers, 7′ × 70′, fired by pulverized coal.

Raw and Clinker Mill (Combined. Any unit may be employed for either raw material or clinker).

4 Bradley-Hercules mills, each driven by 300 H. P. slip ring motor.
4 Traylor tube mills, 7′ × 26′, each driven by 500 H. P. synchronous motor through Cutler hammer 60″ magnetic clutch.
1 Traylor rolls, 16″ × 24″, for clinker.
5 Reinforced concrete blending silos, 17′ diameter × 64′ high, capacity 1,600 barrels each.
1 Gypsum silo, 20′ diameter × 42′ high.

Kiln Room.

3 Vulcan kilns, 10′ × 150′, individual motors, reinforced concrete stacks 96″ × 103′.
Clinker storage, 82′ wide × 195′ long, equipped with 1 Champion 8-ton crane and Blaw-Knox 3-yard clam shell bucket. This is a continuation of the stone storage and equipment duplicates latter.

Fuel Mill.

1 Orton & Steinbrenner Locomotive crane, 18 tons.
1 Fuller-Lehigh dryer, 66″ × 42′, pulverized coal fired.

[1] *Rock Products*, August 25, 1923, p. 21.

Concrete, October, 1924, p. 60, *Cement Mill Edition.*

3 Fuller-Lehigh mills, gear-driven, 42″.
Fuller-Kinyon System for distributing pulverized coal.

Stock and Pack House.

12 Reinforced concrete silos, 32′ diameter × 84′ high, in two rows, capacity 200,000.
3 Bates packers.

No power plant. Power purchased. 2,300 volts employed for large motors and 440 volts for smaller motors.

Buildings are of steel frame, covered with Gunite (stucco) side walls and reinforced concrete tile roof.

Kansas Portland Cement Co.[1]

Raw materials—Limestone and shale. Wet process. Fuel—coal.
Capacity—3,000 barrels daily. Location—Bonner Springs, Kansas.

Crushing Plant.

1 Fairmount roll crusher, 36″.
1 Pennsylvania hammer mill.
Stone storage, equipped with Milwaukee 8-ton overhead traveling crane. A belt in a tunnel beneath the storage also helps reclaim.

Raw Mill.

2 Smidth kominuters, No. 85, driven by 125 H. P. motor.
2 Smidth Trix screens.
2 Smidth tube mills, No. 18, driven by 250 H. P., G. E. super-synchronous motors.
3 Correcting basins with mechanical agitation.
Elevators and screw conveyors handle slurry.

Kiln Room.

3 Kiln feed basins with mechanical agitation.
3 Rotary kilns, 9′ to 8′ × 220′ driven by 50 H. P. motors, concrete chimneys.
3 Coolers, 8′6″ × 78′.

Finishing Mill.

7 Giant Griffin mills, driven by 75 H. P. vertical motors.
2 Allis-Chalmers tube mills, No. 722, driven by 400 H. P. G. E. super-synchronous motors.
Cement handled by Fuller-Kinyon system.

Fuel Mill.

1 Jeffrey single-roll coal crusher.
2 Ruggles-Coles coal dryers driven by 20 H. P. motors.
4 Fuller-Lehigh mills.

[1] *Rock Products,* June 13, 1925, p. 49.

Stock House.

6 Reinforced concrete silos, 32′ diameter × 80′ high, capacity 110,100 barrels.
4 Bates valve packers.
Power is purchased.

Cost of Plant.

The cost of building a modern cement plant will naturally depend on many variables—chief of which are the cost of construction in the locality in which the mill is built, the equipment selected, type of the buildings employed, storage provided for raw materials and cement, whether power is made or purchased, etc. At this writing, the mill itself will cost, exclusive of power plant, about $1.75 to $2.00 per barrel of annual output (daily capacity multiplied by 300). A power plant equipped with waste heat boilers and turbo-generators will add from 50 to 75 cents to this figure. Most going cement plants, however, taking into consideration the value of their raw material deposits, quarry equipment, railroad sidings, locomotives and locomotive cranes, stocks of cement, fuel and supplies on hand, as well as the mill proper, will appraise from $3.00 to $5.00 per barrel of annual output.

In providing for the building of a new mill, where securities must be sold, allowance should be made for brokerage. Working capital should also be provided. Various authorities will have their own ideas as to the amount of the latter, but in general 50 cents per barrel of annual output would be a safe and conservative figure.

The elements entering into the cost of manufacturing a barrel of cement are as follows:

1 Raw Material.
  (a) Limestone.
  (b) Shale, clay, etc.
2 Labor.
  (a) Operating.
  (b) Repairs.
3 Supplies.
  (a) Fuel for burning.

(b) Fuel for power or electric-power.
(c) Fuel for drying.
(d) Gypsum.
(e) Repair parts.
(f) Lubricants.
(g) Dynamite.
(h) Miscellaneous.

4 Administrative.
(a) Mill-office and administration.
(b) Laboratory.

5 Fixed Charges.
(a) Depreciation and obsolescence of mill buildings and machinery.
(b) Depletion of raw materials used.
(c) Insurance and taxes.
(d) Contingencies and reserve.

Cost of Raw Materials.

The cost of quarrying the raw materials varies greatly in different localities. It depends on the hardness of the raw material, the overburden to be removed, the water to be handled and method of doing this, the width, thickness, pitch, etc. of the stone deposit, whether hand or shovel loading is employed, the cost of labor and supplies, etc. The relative amount of material and stripping is the first consideration and naturally it is cheaper to quarry where the latter is relatively small compared with the former. Drilling will cost from 50 to 80 cents per foot for deep well drill work and 1 foot of drilling is equivalent to 20-30 tons of rock or about 2.5 to 4 cents per ton of rock blasted. Dynamite in the east ranges from 5 to 8 cents per ton of rock blasted. Hand loading at present costs about 14 to 18 cents per ton. Shovel loading from 6 to 10 cents per ton. Miscellaneous quarry charges amount to about 5 to 10 cents per ton. The following is probably an average figure for quarrying cement rock.

Drilling and blasting labor	5.0 cts. per ton
Loading (steam shovel)	7.0 cts. per ton
Explosives	7.0 cts. per ton
Miscellaneous supplies and repairs	4.5 cts. per ton
Stripping and miscellaneous	10.5 cts. per ton
Total cost per ton	34.0 cts. per ton

This is equivalent to about 11 cents per barrel of cement.

Labor.

The cost of labor varies greatly in different sections of the country. The cost of unskilled labor can of course be estimated fairly well by any one familiar with local conditions. In general, it may be said that a 2,500 to 3,000 barrel mill will require one employee at the mill (quarry not included) for every 15 to 25 barrels of cement produced per day, or from 1½ to 2½ barrels per man hour. Of the skilled laborers, there will be needed a quarry foreman, drillers, millers, burners, engineers, firemen, packers, mill foremen, machinists on repair work, blacksmiths, etc. Of these the millers, burners, packers, mill foremen and some of the machinists must be experienced in cement mill work, and consequently a new mill, located in a new section must import these men from one of the old established centers of the industry, and, in order to induce these men to leave their homes, must pay them much higher wages than the older mills do. In the east the usual charge for all mill labor (skilled about 50 to 75 cents per hour, unskilled, 35 to 40 cents) is between 12 and 20 cents per barrel.

The list below gives an idea of the force necessary to operate a modern cement mill with a capacity of from 2,500 to 3,000 barrels per day and equipped with all labor saving machinery. In this instance power is purchased and the mill is located in a section where labor is cheap.

LABOR FOR A 3,000-BARREL PER DAY CEMENT MILL

Quarry (8 hours). Well drilling by contract, shovel loading.

1 Quarry foreman @ $150 month	$6.00 per day
2 Shovel engineers @ $175 month	14.00
2 Firemen @ $125 month	10.00
6 Pitmen @ 35¢	16.80

2 Trackmen @ 35¢	5.60	
2 Jack drillers @ 35¢	6.40	
2 Powdermen @ 40¢	6.40	
4 Miscellaneous @ 35¢	11.20	
1 Water boy	2.50	$78.90
1 Locomotive engineer	$5.00	
1 Fireman	3.20	
2 Brakemen	5.60	13.80
Total quarry labor		$92.70
Cost per ton @ 1,000 tons daily		9.3 cents
Cost per barrel at 3.2 barrels to ton		2.9 cents

Crusher Bldg. (10 hours).

1 Hoist man @ 40¢	$3.20	
1 Crusher man @ 30¢	2.40	
1 Hammer mill man @ 40¢	3.20	
1 Assistant @ 30¢	2.40	
1 Oiler @ 35¢	2.80	$14.00

Dryers (10 hours).

1 Dryer man @ 40¢	$4.00	
1 Bin tender @ 30¢	3.00	
1 Oiler and sweeper @ 35¢	3.50	$10.50

Stone Storage (10 hours).

3 Belt tenders @ 30¢		9.00

Mill Room (2 10-hour shifts).

1 General foreman @ $175	$6.00	
2 Millers @ 45¢	9.00	
2 Oilers and bin tenders @ 30¢	6.00	
2 Assistant millers @ 35¢	7.00	28.00

Kiln Building (2 12-hour shifts).

3 Burners @ 50¢	$12.00	
2 Oilers and sweepers @ 30¢	7.20	
2 Bin tenders @ 30¢	7.20	26.40

Clinker Storage (2 10-hour shifts).

2 Crane men @ 50¢	$12.00	
2 Gypsum men @ 50¢	4.80	16.80

Fuel Mill (8 hours).		
1 Miller @ 45¢	$3.60	
1 Fireman @ 30¢	2.40	
1 Laborer @ 30¢ (4 hours)	1.20	$7.20
Machine Shop (10 hours).		
2 Machinists @ 75¢	$15.00	
2 Helpers @ 35¢	7.00	
1 Blacksmith @ 60¢	6.00	
1 Helper @ 35¢	3.50	
1 Repairman quarry cars @ 60¢	6.00	
1 Helper @ 35¢	3.50	41.00
Store House.		
1 Head storekeeper	$5.00	
1 Assistant	3.50	$8.50
Electrical Shop.		
1 Chief electrician	$6.00	
1 Assistant electrician	5.60	
4 Helpers	16.00	27.60
Repair Gang.		
6 Repairmen @ 40¢	$19.20	
1 Master mechanic	8.00	27.20
Yard Gang.		
1 Craneman	$6.00	
6 Laborers	14.40	
1 Team and driver	5.00	
1 Truck driver	4.00	29.40
Miscellaneous Crafts.		
1 Carpenter	$4.00	
1 Helper	3.00	
1 Welder	6.00	
1 Helper	3.00	
1 Babbitting and sheet iron worker	4.00	
1 Helper	3.00	23.00
Laboratory.		
2 Assistant chemists	$12.00	
1 Physical tester	6.00	
2 Sample boys	6.00	24.00

Plant Administration.			
3	General foreman	$20.00	
1	Timekeeper	4.00	
1	Shipping clerk	5.00	
1	Stenographer	4.00	
1	Switchboard girl	3.00	
1	Office boy	2.40	$38.40
	Total		$331.10
	Miscellaneous labor not distributed		20.35
			$351.45
	Cost per barrel in bins based on 2,892 barrels average daily production		12.15 cents
	Add for packing and sack cleaning by contract		4.00 cents
	Labor pack house		1.02 cents
	Total cost per barrel f. o. b. cars		17.17 cents

Supplies and Fuel.

The cost of the supplies, coal, gypsum and limestone or clay, if these have to be purchased, can, of course, be calculated fairly closely. Under favorable conditions, such as soft raw material and a well installed power generation and transmission system, the power necessary to manufacture a barrel of cement can be made with 35 pounds of good coal. Even hard raw materials should not increase this to more than 40 pounds. Low grade fuel, poor engines and boilers and faulty power transmission, however, may easily raise this much higher.

Where waste heat boilers are employed and a modern turbo-generator set is installed practically all the power necessary to operate the plant can be obtained from the waste gases of the kilns. Power obtained from waste heat boilers costs about 0.6 to 0.8 cents per kw-hr. covering interest on investment, operating and maintenance charges. Where power is purchased, the amount of this necessarily will range between 14 and 18 kw-hr. (with an average of 16 kw-hr. per barrel of cement produced for modern equipment). That is to say a 3,000-barrel per day cement mill will manufacture 90,000 barrels per month and use 1,440,000 kw-hr. in so doing.

For the amount of coal used to burn see the chapter on burning.

In general, a barrel of cement can be burned by the dry process in long kilns with about 100 pounds of good coal (14,000 B. t. u. per pound) or 10 gallons of crude oil. A barrel of cement can be burned by the wet process with about 120 pounds of good coal or 12 gallons of oil. Where the coal is of poorer quality than is indicated above proper allowance, on a B. t. u. basis, should be made.

Each barrel of Portland cement has added to it from 8 to 12 pounds of gypsum. The latter is the limit placed by the standard specifications and about 10 pounds is the usual amount required. If plaster of Paris is used in place of gypsum, practically the same amount is required and its cost delivered is usually about twice as great. In the eastern part of the United States, gypsum can generally be obtained f. o. b. the mill at from $5 to $8 per ton.

The cost of lubricants varies greatly, but under good management and careful attention to avoid waste, can be reduced to from 1.0 to 1.7 cents per barrel.

The repair parts form one of the heaviest of the supply items of a cement mill and this item of expense depends, of course, largely on the type of machinery installed to do the grinding. The care with which the machinery is used also has a large influence on this item. Repair parts may cost anywhere from 6 to 10 cents a barrel, even with good management.

The miscellaneous supplies usually foot up to about 2 to 4 cents a barrel. Theoretically, the container in which cement is shipped is supposed to pay for itself and is not included in the cost of mill supplies. The labor of packing and of checking, sorting, cleaning and repairing bags has been indicated under labor.

Administrative Expenses, Depreciation, Etc.

The administrative expenses vary greatly with the size of the mill and the calibre of the men employed. With a small mill employing a first-class manager and chemist and good assistants,

this may figure as high as 15 cents a barrel, while a large mill may reduce this easily to 5 to 8 cents a barrel.

Of the fixed charges, taxes and insurance usually amount to 1 to 2 cents a barrel. The depreciation of mill buildings and machinery is usually figured at 5 per cent of their cost erected, and the interest on bonds, etc., can, of course, be calculated with certainty. To calculate the value of the raw materials used, it is necessary to know the amount of these available, when the calculation becomes merely one for arithmetic.

The cost of manufacturing Portland cement may, therefore, be said to depend on (1) the location of the mill and the ease with which it can obtain its supplies, (2) the cost of labor, fuel, power and gypsum, (3) the efficiency of the machinery installed, (4) the extent, suitability and softness of the raw materials, and (5) the management of the mill and the purchasing of its supplies.

Present Cost of Manufacture.

At the present time the cost of manufacturing cement at a plant located in the central or eastern part of the United States will range somewhat as follows:

Cost of raw materials	10 to 15 cents
Mill labor	
Repair	5 to 8 cents
Operating	12 to 25 cents
Supplies	
Fuel	30 to 45 cents
Gypsum	3 to 4 cents
Lubricants	1 to 2 cents
Repair parts	6 to 10 cents
Miscellaneous	2 to 4 cents
Power (when purchased)	16 to 24 cents
Mill administration	3 to 5 cents
Cost f. o. b. bins	$0.88 to $1.52
Packing, loading and sack expenses	.06 .08
Cost f. o. b. cars	$0.94 to $1.60

The above is, of course, a bare manufacturing cost. To it must be added administrative salaries and expense of the general office and sales force, depreciation and depletion, insurance, taxes and interest charges, reserves, losses, etc. These items will *greatly increase* the above figure.

ANALYTICAL METHODS

CHAPTER XVI

THE ANALYSIS OF CEMENT

Preparation of the Sample[1]

[1] See also Chapter XIX on "The inspection of cement."

The sample is usually received at the chemical laboratory in a paper or cloth bag or in a tin box or can. Here the sample is well mixed by passing several times through a coarse sieve, and by rolling back and forth on a sheet of paper, or better still, one of oil cloth. When thoroughly well mixed it is spread out in a thin layer on the paper, or oil cloth, and divided into 20 to 30 little squares with the point of a spatula or trowel. A small quantity (about 1 or 2 grams) of cement is now taken from each one of these squares with the trowel or spatula point and these small samples are mixed and 5 to 10 grams of the mixture prepared as described in the next paragraph for the chemical analysis. The main portion of the cement is then replaced in the bag or bucket and used for the physical tests.

In order that the solvents used to decompose the cement for analysis may do their work, the portion weighed out must contain no coarse pieces of clinker. To guard against this, pass the smaller sample through a No. 100-mesh test sieve, grinding any residue caught upon the sieve in an agate mortar until it, too, passes. From the size and shape of the ordinary agate mortar and pestle the operation of grinding is very fatiguing. It may be much facilitated, however, by cutting a hole, of such size and shape as to hold the mortar firmly, in the middle of a block of hard wood, a foot or so square. The pestle is then fixed in a piece of round brass tubing of sufficient bore, or else in a round hard wood handle. Several mechanical grinders are on the market, descriptions of which may be found in the trade catalogues of most of the prominent dealers in chemical apparatus.

After being ground the sample for chemical analysis should be placed in a small (one or two ounce) wide mouth bottle and tightly corked. If for immediate use a sample or coin envelope may be substituted for the bottle. The bottles are cheap enough, however, and, as cement rapidly absorbs water and carbon dioxide from the air, it is a good rule to use them altogether.

Standard Specifications for Chemical Properties of Cement.

The following limits shall not be exceeded:[1]

Loss on ignition, per cent	4.00
Insoluble residue, per cent	0.85
Sulphuric anhydride (SO_3), per cent	2.00
Magnesia (MgO), per cent	5.00

Standard Methods for Chemical Analysis

The standard specifications and tests for Portland cement give the following directions for determining loss on ignition, insoluble residue, sulphuric anhydride and magnesia. There are no standard methods for determining the other constituents in cement.

Loss on Ignition

One gram of cement shall be heated in a weighed covered platinum crucible, of 20 to 25-cc. capacity, as follows, using either method (a) or (b) as ordered:

(a) The crucible shall be placed in a hole in an asbestos board, clamped horizontally so that about three-fifths of the crucible projects below, and blasted at a full red heat for fifteen minutes with an inclined flame; the loss in weight shall be checked by a second blasting for five minutes. Care shall be taken to wipe off particles of asbestos that may adhere to the crucible when withdrawn from the hole in the board. Greater neatness and shortening of the time of heating are secured by making a hole to fit the crucible in a circular disk of sheet platinum and placing this disk over a somewhat larger hole in an asbestos board.

(b) The crucible shall be placed in a muffle at any temperature between 900 and 1,000° C. for fifteen minutes and the loss in weight shall be checked by a second heating for five minutes.

[1] Tentative American Standards, A. S. T. M., C9-21.

A permissible variation of 0.25 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 4 per cent.

Insoluble Residue

To a 1-gram sample of cement shall be added 10 cc. of water and 5 cc. of concentrated hydrochloric acid; the liquid shall be warmed until effervescence ceases. The solution shall be diluted to 50 cc. and digested on a steam-bath or hot-plate until it is evident that decomposition of the cement is complete. The residue shall be filtered, washed with cold water and the filter paper and contents digested in about 30 cc. of a 5 per cent solution of sodium carbonate, the liquid being held at a temperature just short of boiling for fifteen minutes. The remaining residue shall be filtered, washed with cold water, then with a few drops of hot hydrochloric acid, 1-9, and finally with hot water, and then ignited at a red heat and weighed as the insoluble residue.

A permissible variation of 0.15 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 0.85 per cent.

Sulphuric Anhydride

One gram of the cement shall be dissolved in 5 cc. of concentrated hydrochloric acid diluted with 5 cc. of water, with gentle warming; when solution is complete 40 cc. of water shall be added, the solution filtered and the residue washed thoroughly with water. The solution shall be diluted to 250 cc., heated to boiling and 10 cc. of a hot 10 per cent solution of barium chloride shall be added slowly, drop by drop, from a pipette and the boiling continued until the precipitate is well formed. The solution shall be digested on the steam-bath until the precipitate has settled. The precipitate shall be filtered, washed and the paper and contents placed in a weighed platinum crucible and the paper slowly charred and consumed without flaming. The barium sulphate shall then be ignited and weighed. The weight obtained multiplied by 34.3 gives the percentage of sulphuric anhydride. The acid filtrate obtained in the determination of the insoluble

residue may be used for the estimation of sulphuric anhydride instead of using a separate sample.

A permissible variation of 0.10 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 2 per cent.

Magnesia

To 0.5 gram of the cement in an evaporating dish shall be added 10 cc. of water to prevent lumping and then 10 cc. of concentrated hydrochloric acid. The liquid shall be gently heated and agitated until attack is complete. The solution shall then be evaporated to complete dryness on a steam or water-bath. To hasten dehydration the residue may be heated to 150 or even 200° C. for one-half to one hour. The residue shall be treated with 10 cc. of concentrated hydrochloric acid diluted with an equal amount of water. The dish shall be covered and the solution digested for ten minutes on a steam-bath or water-bath. The diluted solution shall be filtered and the separated silica washed thoroughly with water. Five cubic centimeters of concentrated hydrochloric acid and sufficient bromine water to precipitate any manganese which may be present, shall be added to the filtrate (about 250 cc.). This shall be made alkaline with ammonium hydroxide, boiled until there is but a faint odor of ammonia, and the precipitated iron and aluminum hydroxides, after settling shall be washed with hot water, once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate shall be transferred by a jet of hot water to the precipitating vessel and dissolved in 10 cc. of hot hydrochloric acid. The paper shall be extracted with acid, the solution and washings being added to the main solution. The aluminum and iron shall then be reprecipitated at boiling heat by ammonium hydroxide and bromine water in a volume of about 100 cc. and the second precipitate shall be collected and washed on the filter used in the first instance if this is still intact. To the combined filtrates from the hydroxides of iron and aluminum, reduced in volume if need be, 1 cc. of ammonium hydroxide shall be added, the solution brought to boiling, 25 cc. of a saturated solution of

boiling ammonium oxalate added, and the boiling continued until the precipitated calcium oxalate has assumed a well-defined granular form. The precipitate after one hour shall be filtered and washed, then with the filter shall be placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner; after ignition it shall be redissolved in hydrochloric acid and the solution diluted to 100 cc. Ammonia shall be added in slight excess and the liquid boiled. The lime shall then be reprecipitated by ammonium oxalate, allowed to stand until settled, filtered and washed. The combined filtrates from the calcium precipitates shall be acidified with hydrochloric acid, concentrated on the steam bath to about 150 cc. and made slightly alkaline with ammonium hydroxide, boiled and filtered (to remove a little aluminum and iron and perhaps calcium). When cool, 10 cc. of saturated solution of sodium-ammonium-hydrogen phosphate shall be added with constant stirring. When the crystalline ammonium-magnesium orthophosphate has formed, ammonia shall be added in moderate excess. The solution shall be set aside for several hours in a cool place, filtered and washed with water containing 2.5 per cent of NH_3. The precipitate shall be dissolved in a small quantity of hot hydrochloric acid, the solution diluted to about 100 cc., 1 cc. of a saturated solution of sodium-ammonium-hydrogen phosphate added, and ammonia drop by drop, with constant stirring, until the precipitate is again formed as described and the ammonia is in moderate excess. The precipitate shall then be allowed to stand about two hours, filtered and washed as before. The paper and contents shall be placed in a weighed platinum crucible, the paper slowly charred, and the resulting carbon carefully burned off. The precipitate shall then be ignited to constant weight over a Meker burner, or a blast not strong enough to soften or melt the pyrophosphate. The weight of magnesium pyrophosphate obtained multiplied by 72.5 gives the percentage of magnesia. The precipitate so obtained always contains some calcium and usually small quantities of iron, aluminum, and manganese as phosphates.

A permissible variation of 0.4 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 5 per cent.

DETERMINATION OF SILICA, FERRIC OXIDE AND ALUMINA, LIME AND MAGNESIA

Method Proposed by the Committee on Uniformity in the Analysis of Materials of the Portland Cement Industry of the New York Section of the Society of Chemical Industry[1]

Solution

One-half gram of the finely powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited in a covered platinum crucible over a strong blast for fifteen minutes, or longer if the blast is not powerful enough to effect complete conversion to a cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, moistened with enough water to prevent lumping, and 5 to 10 cc. of strong HCl added and digested with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod.[2] The solution is then evaporated to dryness, as far as this may be possible on the bath.

Silica

The residue without further heating is treated at first with 5 to 10 cc. of strong HCl which is then diluted to half strength or less, or upon the residue may be poured at once a larger volume of acid of half strength. The dish is then covered and digestion allowed to go on for ten minutes on the bath, after which the solu-

[1] This committee consisted of Messrs. Clifford Richardson, Spencer B. Newberry and H. A. Schaffer. Their various reports were published in *Journal of the Society of Chemical Industry*, XXI, **12**, 830 and 1216, *Journal American Chemical Society*, XXV, **1180**, and XXVI, 995; and *Cement and Engineering News*, XVI, 37.

[2] If anything remains undecomposed it should be separated, fused with a little Na_2CO_3 dissolved and added to the original solution. Of course, a small amount of separated non-gelatinous silica is not to be mistaken for undecomposed matter.

tion is filtered and the separated silica washed thoroughly with water. The filtrate is again evaporated to dryness, the residue without further heating, taken up with acid and water and the small amount of silica it contains separated on another filter-paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for fifteen minutes and checked by a further blasting for ten minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 cc. of HFl and four drops of H_2SO_4 and evaporated over a low flame to complete dryness. The small residue is finally blasted, for a minute or two, cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.[1]

Iron Oxide and Alumina

The filtrate, about 250 cc., from the second evaporation for SiO_2, is made alkaline with NH_4OH after adding HCl, if need be, to insure a total of 10 to 15 cc. strong acid, and boiled to expel excess of NH_3, or until there is but a faint odor of it, and the precipitated iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl, the solution passing into the beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by NH_4OH, boiled and the second precipitate collected and washed on the same filter used in the first instance. The filter-paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted five minutes, with care to prevent reduction, cooled and weighted as $Al_2O_3 + Fe_2O_3$.[2]

[1] For ordinary control work in the plant laboratory this correction may, perhaps, be neglected; the double evaporation never.

[2] This precipitate contains TiO_2, P_2O_5, Mn_3O_4.

Lime

To the combined filtrate from the $Al_2O_3 + Fe_2O_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 20 cc. of a saturated solution of ammonium oxalate are added, and the boiling continued until the precipitated CaC_2O_4 assumes a well-defined granular form. It is then allowed to stand for twenty minutes, or until the precipitate has settled, and then filtered and washed. The precipitate and filter are placed wet in a platinum crucible, and the paper burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl, and the solution made up to 100 cc. with water. Ammonia is added in slight excess, and the liquid is boiled. If a small amount of Al_2O_3 separates this is filtered out, weighed, and the amount added to that found in the first determination, when greater accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, filtered, and washed,[1] weighed as oxide by ignition and blasting in a covered crucible to constant weight, or determined with dilute standard permanganate.[2]

Magnesia

The combined filtrates from the calcium precipitates are acidified with HCl and concentrated on the steam-bath to about 150 cc., 10 cc. of saturated solution of $Na(NH_4)HPO_4$ are added, and the solution boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice-water. After cooling, NH_4OH is added drop by drop with constant stirring until the crystalline ammonium-magnesium ortho-phosphate begins to form, and then in moderate excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot dilute HCl, the solution made up to about 100 cc., 1 cc. of a saturated solution of $Na(NH_4)HPO_4$ added, and ammonia drop by drop, with constant stirring until the precipitate

[1] The volume of wash water should not be too large; vide Hillebrand.

[2] The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

is again formed as described and the ammonia is in moderate excess. It is then allowed to stand for about two hours when it is filtered on a paper or a Gooch crucible, ignited, cooled and weighed as $Mg_2P_2O_7$.

Method Proposed by the Committee on the Uniform Analysis of Cement and Cement Materials of the Lehigh Valley Section of the American Chemical Society[1]

Silica

Weigh out 0.5 gram into a wide platinum dish of about 50-cc. capacity; add a very little water and break up lumps with a glass rod; add 5 cc. hydrochloric acid (1 : 1) and evaporate to dryness at a moderate heat, continuing to heat the mass—not above 200° C.—until all odor of acid is gone. Do not hurry this baking or skimp the time. The whole success of the analysis depends on thoroughness at this point. Cool; add 20 cc. hydrochloric acid (1 : 1); cover and boil gently for ten mintes; add 30 cc. water, raise to boiling, and filter off the silica; wash with hot water four or five times; put in crucible, ignite (using blast for ten minutes), and weigh as SiO_2.

Iron and Alumina

Make filtrate alkaline with ammonia, taking care to add only slight excess; add a few drops of bromine water and boil till odor of ammonia is faint. Filter off the hydroxides of iron and aluminum, washing once on the filter. Dissolve the precipitate with hot dilute nitric acid, reprecipitate with ammonia; boil five minutes; filter and wash the iron and alumina with hot water once; place in crucible, ignite carefully, using blast for five minutes, and weigh combined iron and aluminum oxides.

[1]This committee was appointed at a meeting of the Lehigh Valley Section of the American Chemical Society, held November 18, 1903, and consisted of Messrs. Wm. B. Newberry, Richard K. Meade and Ernest B. McCready. Their report was published in *Cement and Engineering News*, August, 1904, and embodies the methods most acceptable to the chemists actively employed in the cement industry as ascertained by correspondence with these chemists themselves.

Lime

Make the filtrate from the hydroxides alkaline with ammonia; boil; add 20 cc. boiling saturated solution ammonium oxalate; continue boiling for five minutes; let settle and filter. Wash the calcium oxalate thoroughly with hot water using not more than 125 cc., and transfer it to the beaker in which it was precipitated, spreading the paper against the side and washing down the precipitate first with hot water and then with dilute sulphuric acid (1 : 4); remove paper; add 50 cc. water, 10 cc. concentrated sulphuric acid, heat to incipient boiling and titrate with permanganate,[1] calculating the CaO.

Magnesia

If the filtrate from the calcium oxalate exceeds 250 cc., acidify, evaporate to that volume; cool, and when cold add 15 cc. strong ammonia and with stirring 15 cc. stock solution of sodium hydrophosphate. Allow to stand in the cold six hours or preferably over night; filter; wash the magnesium phosphate with dilute ammonia (1 : 4 + 100 gms. ammonium nitrate per liter) put in crucible, ignite at low heat and weigh the magnesium pyrophosphate.

NOTES

Of the above schemes, the first is undoubtedly the more accurate of the two. It does not seem practicable, however, to use it in the everyday routine work of the mill laboratory. It also requires a high degree of manipulative skill to carry out the additional steps in its performance. When very accurate determinations are required, it will undoubtedly give better results than the second scheme, provided the analysis is skillfully executed. On the other hand, under the conditions usually met with in the laboratories of cement manufacturers and large users, where rapidity, coupled with a moderate degree of accuracy is required, and where one man is required to run a number of analyses per day, the second scheme will unquestionably give more satisfaction, if properly carried out. A combination of the two schemes which will usually be found as far as the general run of analysts would care to go towards using the first scheme, consists in determining silica as directed by the first scheme, without, however, purifying the silica with

[1] See "Volumetric Determination of Lime," page 451.

hydrochloric and hydrofluoric acids, and then the other elements by the second scheme. This adds to the accuracy of the latter and is not so tedious as the first.

A good well-made Portland cement is practically entirely soluble in hydrochloric acid. Fusion, therefore, with sodium or potassium carbonate is rarely necessary. It is also objectionable, for when calcium and magnesium are precipitated, as oxalate and phosphate respectively, from solutions containing much sodium or potassium salts, the precipitates are almost sure to be contaminated with alkaline salts. Even much washing fails to remove the impurity from the precipitate. When, therefore, the sample of cement has been fused directly with from 3 to 5 grams of sodium carbonate, there is sure to be this danger that the lime and magnesia precipitates will carry down some sodium salts, from which subsequent washing will fail to free them. In accurate work this error can be eliminated by reprecipitation. If instead of fusing the sample directly with five to ten times its weight of sodium carbonate, the impure silica, separated by treatment with hydrochloric acid, is fused with an equal bulk of sodium carbonate, the quantity of sodium salts introduced into the solution will be reduced to one-fourth, usually between 1.0 and 1.5 grams of sodium chloride.

Should the cement prove to leave a considerable residue of silicious matter on dissolving in acid, the best plan will be to weigh out a new sample and pursue the following method suggested by Dr. Porter W. Shimer, Easton, Pa.:

Weigh ½ gram of the finely ground dried cement into a platinum crucible and mix intimately, by stirring with a glass rod, with 0.5 gram of pure dry sodium carbonate. Brush off the rod into the crucible with a camel's hair brush. Cover the crucible and place over a low flame. Gradually raise the flame until the crucible is red hot and continue the heating for five minutes longer; then place over a blast lamp and heat five minutes more. While still hot, plunge the bottom of the crucible half the way up into cold water. This will loosen the mass. Drop the mass into a casserole or dish and cover the latter with a watch-glass. Pour into the crucible a portion of a mixture of 30 cc. of hot water and 10 cc. of dilute hydrochloric acid. Heat on a hot plate, and then pour into the dish or casserole. Clean out the crucible with a rubber-tipped rod, using the rest of the acid and water. The quantity of sodium salts introduced into the solution from 0.5 gram of carbonate is so small that possible contamination of the lime and magnesia precipitates is done away with. On heating cement and sodium carbonate together in this proportion no fusion takes place, only a sintering.

The above method of procedure will be found useful also in analysis of Rosendale or Natural cement, hydraulic limes, slag cement, puzzolana and the so-called "Iron-cements."

The amount of residue left on solution with acid is considered to be a test of the thoroughness with which the cement has been made. Peckham uses a 10 per cent solution of hydrochloric acid and 5 grams of cement just as received, making the solution slowly and with care. Blount dissolves the cement in strong hydrochloric acid, evaporates the solution to dryness, but not intentionally baking the evaporated material, redissolves in hydrochloric acid, filters, washes, dissolves the precipitated silica with sodium carbonate solution and collects, ignites and weighs the final insoluble residue. In carrying out this test, the standard method should be followed carefully as variations in the method of manipulation will give different results.

The quantity of silica which will be left on treating cement with acid will depend not only upon the chemical composition of the cement, but also upon the fineness to which the sample is ground, strength of acid, etc., coarsely ground material giving much more residue than finely ground. Cement passing a 50-mesh sieve, but retained by a 100, will give much more silica than that passing a 100-mesh, but retained on a 200-mesh, yet neither has binding properties in the ordinary sense of the word, so that the contention made that the silica which does not dissolve even though it may come from good properly burned material, still comes from inert particles, and is therefore not in a form of active combination, is not logical because by grinding these inert particles a little finer we can considerably reduce the silica left without increasing any of their hydraulic value. Many silicates are also soluble in acid, which have no hydraulic properties, such as slags, so that all the silica which goes into solution is not necessarily combined in such a way as to form hydraulic compounds.

The test does not seem to the writer to be of much practical value. Of course, when the residue of uncombined silica is large, it shows something is wrong with the cement, but this fact is usually revealed much more satisfactorily by the tests for soundness which property is dependent on the proper combination of the silica with the lime. A marl containing a per cent or so of silica in the form of quartz grains would probably give a cement containing from ½ to 1 per cent of insoluble or uncombined silica, yet if this quartz had been taken into consideration in proportioning the raw materials, this cement might easily be better than one which gives no free or uncombined silica, because the latter might be unsound. Also, as we have said before, all the silica, which is reported as combined is not necessarily so combined as to form Portland cement.

At the mill itself, there is little knowledge to be gained by the test, as the soundness test, coupled with the usual determinations, will tell whether the fault is due to careless manufacture or improper proportioning of the raw materials.

Alex. Cameron,* in 1894, pointed out the fact that no matter how many evaporations were made in determining silica, accurate results could not be obtained unless a filtration intervened between each one. This paper seems to have escaped the notice of most chemists and was only brought to their knowledge by Dr. W. F. Hillebrand,[1] in 1901, in a paper read at a meeting of The American Chemical Society, in Philadelphia, in December of that year, in which he gave the results of his own experiments along that line. It was in accordance with his suggestion that the committee of the New York Section of the Society of Chemical Industry advised the double evaporation with intervening filtration, which they inserted in their scheme. There is no question but that Dr. Hillebrand is right and that this procedure is necessary in very accurate work. In the analysis of Portland cement, a residue of silica, amounting to from two to four milligrams, can usually be obtained by evaporation of the filtrate from the first silica precipitate to dryness, still the extra step is tedious, and adds considerably to the time necessary for making an analysis. It is also true, however, that there is considerable iron and alumina carried down with the silica, and that these two errors will balance each other to a great extent, so that the amount of silica reported is seldom more than one or two-tenths of a per cent low. Below are some figures upon this.

Cement No.	A Per cent silica after one evaporation and dehydration at 200° C.[2]	B Impurities in this precipitate.	C Additional silica recovered by a second evaporation.	D Silica in the iron and alumina precipitate.	E Total silica, columns (A + C + D) − B.[3]	Error in column A.
1	19.95	0.35	0.38	0.09	20.07	−0.12
2	20.18	0.31	0.42	0.12	10.41	−0.23
3	20.46	0.37	0.36	0.08	29.53	−0.07
4	21.12	0.38	0.25	0.05	20.03	+0.09
5	21.63	0.34	0.32	0.14	21.75	−0.12
6	22.45	0.41	0.34	0.01	22.49	−0.04

* *Chem. News*, LXIX, 171.

[1] *Jour. Amer. Chem. Soc.*, XXIV, 362.

[2] This represents the silica which would be found by the method of the committee of the Lehigh Valley Section of the American Chemical Society.

[3] This represents the silica actually present in the sample.

Silica is hard to wash and retains alkalies tenaciously. It is well for the inexperienced operator, until he finds out how much washing is required, to test with silver nitrate, and continue the operation until the washings cease to react for chlorides.

Silica may be ignited wet, but care must be taken not to dry the precipitate too quickly over the flame, else the steam in escaping will carry with it fine particles of silica. The best plan is not to place the crucible at first directly over the burner, but instead to one side of a low flame. The silica must be ignited over a blast lamp in order to drive off the last traces of water, which it holds most tenaciously. Ignition over a Bunsen burner, even for some hours, is insufficient for complete dehydration. The blast-lamp will also help to burn off the last trace of the carbon of the filter-paper.

The purity of the silica can easily be tested, and indeed in accurate work, it should always be done. After burning off the carbon, igniting over a blast and accurately weighing, moisten the silica with dilute sulphuric acid and then half fill the crucible with C. P. hydrofluoric acid. Incline the crucible on a tripod over a burner turned low, in such a way that the flame plays under the upper part of the crucible. This causes a rapid evaporation of the solution. When no more fumes come from the crucible move the burner back until it plays upon the bottom of the crucible and raise the flame until the crucible is cherry-red. Cool and weigh. The loss represents silica, SiO_2, and the residue in the crucible is usually alumina. Its weight may be added to that of the iron and alumina found by precipitation with ammonia, or the residue may be dissolved in concentrated hydrochloric acid and added to the filtrate from the silica, before the addition of ammonia.

If silica is to be purified, however, it is also necessary, not only to make the double evaporation with intervening filtration, but also to determine the silica in the iron and alumina and add it to the weight of the purified silica. Unless this is done the silica will be too low and the iron and alumina too high.

Alumina, Al_2O_3, is soluble to some extent in a large excess of ammonia. If, however, the excess is expelled by boiling, the alumina is again precipitated. The presence of ammonium chloride in the solution greatly aids in the separation of alumina by ammonia. The precipitate of iron and alumina must be filtered off promptly since the alkaline liquid will absorb carbon dioxide from the air, forming calcium carbonate which would be filtered off with the iron and alumina. For the same reason, when for any cause the filtrate from the iron and alumina has to stand some days, it should be acidified with hydrochloric acid before setting aside. This is necessary when the calcium is to be determined volumetrically, and it saves trouble elsewhere, since the deposit of calcium carbonate forms as a crust on the sides and bottom

of the beaker, and is very difficult to remove, without solution and reprecipitation.

To avoid time lost in boiling off a large excess of ammonia, only a very slight excess of this reagent should be added. The bottle shown in Fig. 130 will be found very useful in ammonia precipitations, as the addition can be made drop by drop, if desired, and the quantity added regulated so as to give the liquid only a faint odor of ammonia.

Magnesium hydroxide, $Mg(OH)_2$, is not completely soluble in ammonia. The precipitate is, however, readily soluble in ammonia solutions, containing sufficient ammonium chloride. The precipitation of the magnesia along with the iron and alumina is insured against by the formation of ammonium chloride which takes place before the iron and alumina are precipitated, on adding ammonia to the hydrochloric acid solution. If preferable the operator can be on the safe side by adding half a gram of the salt itself (ammonium chloride) to the filtrate from the silica before precipitating the iron and alumina. The presence of ammonium chloride is also necessary for the complete precipitation of the alumina.

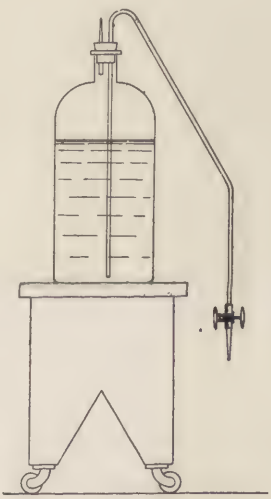


Fig. 130.—Apparatus for Ammonia Precipitations.

The precipitate of iron and alumina always contains more or less lime and magnesia, from which long washing fails to free it. Solution and reprecipitation are, therefore, necessary to get around the difficulty. The precipitate is very apt to contain traces of silica also.

Some of this comes from the action of the ammonia on the reagent bottle in which it is kept, some from the action of the alkaline liquid on the beaker in which the precipitation was made, and some which failed to be separated by evaporation in the proper place is also carried down here. Since the impurity usually present in the silica is alumina and that in the alumina is silica, the two sources of error tend to balance each other. If desired the weighed precipitate of ferric oxide and alumina can be dissolved by fusion with potassium bisulphate for some hours, the fused mass dissolved in water, a few drops of sulphuric acid added and the solution evaporated until fumes come off in quantity. The residue is then collected after cooling and diluting the solution,[1] and weighed as SiO_2.

Ammonia water takes up silica rapidly from the glass container, hence when accurate work is desired and purification of silica and alumina are to be undertaken; it is necessary to redistill the ammonia over lime. This should be done every week or two at least. Even for technical work it is not a bad plan, as there is no telling how long the ammonia has stood on some dealer's shelves. The still may be kept set up in a corner of the hood and the operation conducted by the laboratory boy. By using redistilled ammonia it is possible to do away with the second precipitation of the iron and alumina, which is made necessary by the presence of ammonium carbonate in the ammonia water, as this carbonate precipitates some calcium carbonate along with the alumina. Of late years the author has been able to purchase ammonia water contained in wax bottles. This of course has had no chance to take up silica and the trouble of redistilling is saved.

The precipitate of iron and alumina is troublesome to wash, and unless it is freed from chlorides, some loss of iron, by volatilization as ferric chloride, will result when the precipitate is ignited. In order to avoid this tedious washing, the writer has always followed the plan of dissolving the first precipitate in nitric acid, thus avoiding the presence of chlorides in the second precipitate and doing way with the tedious washing. When this is done only enough washing is necessary to collect the precipitate in the point of the filter. This plan is suggested in the method of the Lehigh Valley Committee.

Calcium oxalate may be washed with hot water. Some chemists prefer to add a little ammonia to the wash water, but to the author this seems unnecessary. The precipitate should always be formed in a boiling ammoniacal solution, with stirring, and allowed to settle before filtering. Some chemists heat the ammonium oxalate solution also to boiling before adding to the boiling solution containing the calcium. Sufficient ammonium oxalate should always be added to convert all the magnesium present as well as the calcium to oxalate, else the precipitation of the

[1] Hillebrand, *Jour. Amer. Chem. Soc.*, XXIV, 369.

calcium will be incomplete. Nothing is gained by allowing the lime more than fifteen or twenty minutes to settle.

Magnesium oxalate is not very soluble and if magnesia is present in large amount will be precipitated with the lime. On the other hand, calcium oxalate is slightly soluble in hot water. As cement contains such a small percentage of magnesia the quantity carried down with the lime is usually less than 0.1 per cent, and as the quantity of calcium oxalate which goes into solution is precipitated with the magnesia, the two errors tend to balance each other. The factors entering into a clean separation of lime and magnesia are that there must be an excess of ammonium oxalate and that the solution should measure at least 300 cc.

Directions for making the solution for determining lime volumetrically and for carrying out the process will be found on page 451. The volumetric determination is very accurate and under ordinary technical conditions, when many analyses are made every day, will prove as trustworthy as the gravimetric. When an occasional determination only is made the latter will prove more useful.

Calcium oxalate on ignition over a burner to very faint redness changes to calcium carbonate. If the heating is increased and the blast is used calcium oxide is formed. Instead of weighting as the oxide some chemists prefer to weigh as a sulphate. To do this,[1] dry the precipitate perfectly, detach it as far as possible from the filter to a piece of black glazed paper. Burn the filter-paper in a weighed platinum crucible, and when all carbonaceous matter is burned, brush the precipitate into the crucible from the glazed paper. Drop concentrated sulphuric acid on the precipitate till it is well moistened, avoiding an excess, and heat the crucible under a hood cautiously, from a burner held in the hand, until the swelling of the mass subsides and the excess of sulphuric acid has been driven off, as shown by the disappearance of the white fumes coming from the crucible. Then heat for five minutes to a cherry-red heat, but do not use the blast. Cool and weigh as calcium sulphate, which multiplied by 0.41195 gives the equivalent of lime CaO.

Mr. W. H. Hess uses the following method[2] for converting the calcium oxalate to calcium sulphate. After burning off all the carbon of the filter-paper, the crucible is allowed to cool partly, when a portion of chemically pure dry ammonium nitrate, approximately equal in bulk to the lime in the crucible, and about twice as much chemically pure fused ammonium sulphate are added. A tight-fitting cover is now placed on the platinum crucible and then gentle heat is applied. Mr. Hess found it very convenient to incline the crucible at an angle of 30°, allowing the tip of the crucible cover to project outward, and then apply the

[1] Lord, "Notes on Metallurgical Analysis," p. 11.

[2] *Jour. Amer. Chem. Soc.*, **22**, 477.

flame to the tip of the cover, gradually bringing the flame under the crucible as the reaction grows less and less violent. The reaction is complete when fumes of ammonia salts are no longer driven off. Intense ignition is unnecessary and is to be avoided. The crucible should be weighed with its cover.

The evaporation of the filtrate from the lime may be rapidly carried out, in a large porcelain dish, in the following manner: Place a piece of wire gauze on a tripod and in the center of this, lay a disk of asbestos paper, the size of a silver dollar. Now set the dish on the gauze and place a Bunsen burner, with its flame turned low, so that the latter comes under the asbestos. The solution will then evaporate rapidly, and yet without ebullition, or loss by spurting.

Magnesium pyrophosphate is quite soluble in hot water, less so in cold water, and practically insoluble in water rendered strongly ammoniacal. It should be washed, therefore, with a mixture of water and ammonia. Some chemists use no ammonium nitrate in their washing fluid, and mix in proportions varying from ten to three parts water for one part of ammonia. It is a difficult precipitate to ignite perfectly white, but the blast-lamp should never be used in the attempt to make it so, as destruction of the platinum crucible might follow. The precipitate may be ignited wet if a low flame is used at first.

A Gooch crucible may be used in place of a filter-paper, although it is much less convenient. It consists of a flat-bottomed, perforated crucible provided with a cap (Fig. 131). The perforated crucible is placed in one end of a piece of soft rubber tubing of large bore, the other

Fig. 131.—Gooch crucible.

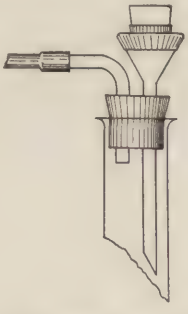


Fig. 132.—Gooch crucible in use.

end of which is stretched over a small funnel passing into a flask through a rubber stopper (Fig. 132). The flask is connected with the filter-pump. To prepare the filter, pour a little prepared asbestos (purified by washing with hot concentrated hydrochloric acid) suspended in

water into the crucible and attach the suction to the flask. The asbestos at once forms a thick felt over the bottom of the crucible, which by using the suction may be readily washed with water. After washing, suck as dry as possible with the pump, remove from the funnel, detach any pieces of asbestos that may be on the outside of the bottom of the crucible, cap, ignite, and weigh. Remove the cap, attach to the funnel as before, apply the suction and pour the liquid to be filtered through the crucible, wash, cap, dry, if necessary, ignite and weigh as before. The crucible and cap may be purchased from dealers in platinum or chemical ware.

The use of platinum dishes is recommended for the solution and evaporation of the sample because platinum is a much better conductor of heat than porcelain and glass, and consequently evaporations can be carried out much more rapidly in them than in anything else. Silica also sticks to porcelain and even to some extent to glass and it is impossible to remove it all from glass or porcelain dishes by rubbing. It does not stick to platinum dishes, however. With silica determinations made in anything but platinum, results are, therefore, too low. If the former ware must be used, the silica which sticks should be dissolved in ammonia water and reprecipitated by acid and added to the main body of the silica on the paper. There is also no danger of contaminating the analysis with silica from the dish when platinum is used. Glass dishes are to be preferred to porcelain dishes where platinum is considered too expensive.

Crucibles in which silica, iron and alumina and barium sulphate have been ignited may be most conveniently cleaned by boiling in them a little hydrofluoric acid. Ignited magnesium pyrophosphate may be readily removed from platinum or porcelain crucibles by placing the latter in a beaker of 10 per cent hydrochloric acid and boiling. The dilute acid in this case will do the work when strong acid will fail. No appreciable loss in weight of the crucible will be occasioned by any of the above treatments.

VOLUMETRIC DETERMINATION OF LIME

Preparation of the Standard Permanganate

Dissolve the quantity of pure crystallized potassium permanganate shown in the table below, in the desired amount of water, using a balance accurate to at least 0.5 per cent. of the weight of permanganate to be taken, and measuring the water with a graduated flask. In this way, a solution can be made of sufficiently near the correct strength for the use of the table in the appendix.

TABLE XLI.—For Preparing Standard Permanganate of Approximately the Strength 1 cc. = 0.005 Gram CaO.

5.64	grams	$KMnO_4$	to	1	liter	of	water
11.28	"	"	"	2	"	"	"
16.92	"	"	"	3	"	"	"
22.56	"	"	"	4	"	"	"
28.20	"	"	"	5	"	"	"
33.84	"	"	"	6	"	"	"
39.48	"	"	"	7	"	"	"
45.12	"	"	"	8	"	"	"
50.76	"	"	"	9	"	"	"
56.40	"	"	"	10	"	"	"

The simplest way to make the solution, is to weigh out the permanganate and place in the bottle with the water, some week or ten days before the solution is to be standardized. The contents of the bottle, which is kept in a dark place, is shaken every now and then for the first two or three days. When the solution is needed, it is siphoned off into another bottle, leaving about an inch of solution in the old bottle. A glass siphon is used and its end should not extend nearer than an inch from the bottom of the bottle. The solution in the new bottle is now shaken and standardized. The writer in his laboratory uses eight-liter (two-gallon bottles) and this quantity of permanganate will last him from two or three weeks. The solution should be standardized every week. It will be found more convenient to make the solution as above and standardize every week, than to attempt to make a solution which will not change, by boiling and filtering as directed by Morse.[1]

The permanganate solution should be kept in a dark place. Fig. 133 shows the arrangement for storing and using the permanganate adopted by the writer.[2]

Standardizing the Permanganate

To standardize the permanganate, weigh into a 400 cc. beaker 0.5 gram of powdered calcite; add 100 cc. of water and 10 cc. of hydrochloric acid, cover with a watch-glass and boil until all carbon dioxide is expelled. When completely dissolved, dilute

[1] *Amer. Chem. Jour.*, XVIII, 401.

[2] *Chemical Engineer*, I, 288.

to the usual volume in which the lime precipitation is made in an analysis, and make alkaline with ammonia. Add 20 cc. of a boiling saturated solution of ammonium oxalate, continue boiling and stirring for a few minutes, let settle, filter and wash thoroughly with hot water using not more than 125 cc. of the liquid. Transfer the filter and precipitate to the beaker in which the precipitation was made, spreading the paper against the side and

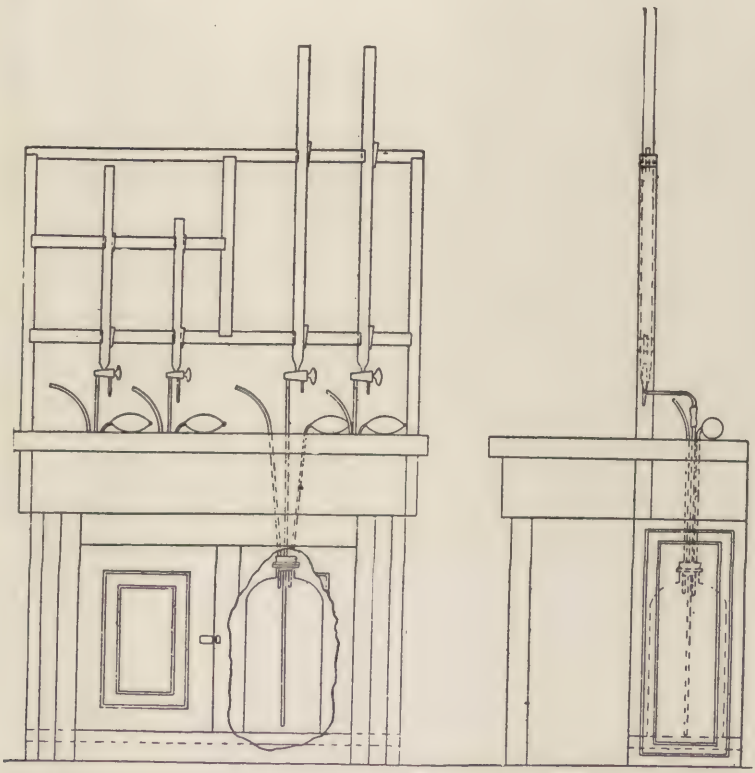


Fig. 133.—Table for titrations.

washing down the precipitate first with hot water and then with dilute sulphuric acid (1:4). Remove the paper, add 50 cc. of water and 10 cc. concentrated sulphuric acid, heat to incipient

boiling and titrate with permanganate. The factor for lime, CaO, is found by dividing 0.56 by the number of cubic centimeters of permanganate taken and for calcium carbonate, $CaCO_3$, by dividing 100 by the number.

The above method is that recommended by the Committee of the Lehigh Valley Section of the American Chemical Society on the Uniform Analysis of Cement and Cement Materials. Some operators prefer to use ferrous ammonium sulphate for standardizing. The usual method of using this is as follows:

Weigh into each of two beakers 1.4 grams of pure crystallized ferrous ammonium sulphate, add cold water, allow the salt to completely dissolve without stirring and then add 10 cc. of dilute sulphuric acid. Stir and run in the permanganate from a burette until the color of the solution in the beaker just changes to pink. The weight of the double salt used divided by 14, and then by the number of cubic centimeters of permanganate required, will give the lime, CaO, value per cubic centimeter, for the permanganate. The duplicate titrations should check closely; if not, another pair should be run. For other methods of standardizing the permanganate solution see "Determination of Ferric Oxide."

The writer has lately used sodium oxalate prepared as directed by Sörensen[1] for standardizing permanganate and found it both convenient and accurate. Theoretically, 0.6697 gram of this salt are equivalent to 0.5 gram of calcium carbonate. In practice the writer has usually found slightly more required and prefers therefore to determine the exact amount by comparing it with calcite or standard sample of cement or limestone. Thus if 0.5 gram of calcite requires 56.5 cc. of permanganate and 0.6700 gram of sodium oxalate 56.4 cc. Then 0.6711 gram of sodium oxalate are used for standardizing thereafter. In use, the salt is dissolved in water, 10 cc. of dilute (1:1) sulphuric acid added, the solution heated to 60° C. and titrated with the permanganate to be standardized.

[1] This may be obtained from the U. S. Bureau of Standards.

The Determination

Directions for precipitating the lime are given on page 269. The writer prefers to make this titration in the following manner: Remove the filter from the funnel, open and lay against the side of the beaker in which the precipitation was made, wash the precipitate from the paper into the beaker with hot water, fold the paper over and allow to remain against the walls of the beaker. Add dilute sulphuric acid to the contents of the beaker, heat the solution to 80° C. and titrate rapidly with standard permanganate until a pink color is obtained, now drop in the filter paper, stir until the color is discharged and finish the titration carefully drop by drop. This procedure allows rapid titration without danger of over-running the end point. The oxalate left in the pores of the paper is usually sufficient to take care of 2 or 3 cc. of standard permanganate.

NOTES

The method depends upon the reaction between oxalic acid and potassium permanganate.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_6 + 8H_2O.$$

The reaction between iron and permanganate is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Hence 5 molecules $H_2C_2O_4$ = 2 mols. $KMnO_4$ = 10 mols. $FeSO_4$ or 5 mols. $H_2C_2O_4$ (= 5 mols. CaO) = 10 mols. $FeSO_4$ (= 10 atoms Fe).

Then 5 mols. CaO = 10 atoms Fe, and 5(40 + 16) CaO = 10 × 56 Fe, or 280 CaO = 560 Fe.

Hence, CaO : Fe :: 280 : 560, from which $CaO = \frac{280}{560}$ Fe or $\frac{1}{2}$ Fe.

So the iron value of any permanganate solution divided by 2 will give its lime value.

The titration with permanganate must be made with a hot solution, between 60° and 70° C. In the scheme given, the solution is heated by the action with the strong sulphuric acid, added just before titration.

Calcite in the form of Iceland Spar can be obtained of great purity, and may be generally taken as 100 per cent $CaCO_3$. In purchasing a new lot it should be specified that the purest grade is wanted "for standardizing." On receipt it should be powdered to pass a 100-mesh sieve and kept in a glass stoppered bottle. From this a small portion should be taken and placed in an ounce wide mouth bottle, provided with either a glass or rubber stopper. This small sample should be dried

at from 100-110° C., and on removal from the drying oven kept tightly stoppered. The calcite should then be checked by a careful analysis for silica, iron oxide and alumina and the lime determined gravimetrically as on page 440. A blank should be run at the same time; that is, a dish is selected and acid added to it just as if it contained a sample, etc. The small residues found after each step should be deducted from those found on analysis of the calcite. The sample used in the writer's laboratory gave less than 0.1 per cent impurities when treated in this manner. The small sample of calcite should be dried after the bottle has been opened for five or six determinations, as it will take up some moisture from the air.

Rapid Determination of Lime Without Separation of Silica, Etc.[1]

Weigh 0.5 gram of cement into a dry 500 cc. beaker and add, with constant stirring, 20 cc. of cold water. Break up the lumps and when all the sample is in suspension, except the heavier particles, add 20 cc. of dilute (1 : 1) hydrochloric acid and heat until solution is complete. This usually takes five or six minutes. Heat to boiling and add dilute ammonia (0.96 sp. gr.) carefully to the solution of the sample until a slight permanent precipitate forms. Heat to boiling and add 10 cc. of a 10 per cent solution of oxalic acid. Stir until the oxide of iron and alumina are entirely dissolved and only a slight precipitate of calcium oxalate remains. Now add 200 cc. of boiling water and sufficient (20 cc.) saturated solution of ammonium oxalate to precipitate the lime. Boil and stir for a few moments, remove from the heat, allow the precipitate to settle and filter on an 11 cm. filter. Wash the precipitate and paper ten times with hot water using not more than 10 or 15 cc. of water each time. Remove the filter from the funnel, open and lay against the sides of the beaker in which the precipitation was made, wash from the paper into the beaker with hot water, add dilute sulphuric acid, fold the paper over and allow to remain against the walls of the beaker. Heat to 80° C. and titrate with standard permanganate until a pink color is obtained, now drop in the filter-paper, stir until the color is discharged and finish the titration carefully drop by drop.

[1] *Chemical Engineer*, I, 21.

NOTES

The above method for the determination of lime is dependent on the fact that lime can be completely precipitated as oxalate in solutions containing free oxalic acid, while iron, alumina and magnesia are not. The method as outlined above was worked out by the writer some years ago and has been in constant use in the laboratories of many large cement companies since that time, giving entire satisfaction.

The oxalic acid method is much more accurate than the one sometimes used of precipitating the iron and alumina by ammonia and then without filtration throwing down the lime as oxalate in the same solution, since in the latter method some of the lime is thrown down as carbonate and hence not found by the permanganate. It is just as rapid as the above because the only extra step is the addition of 10 cc. of oxalic acid solution which is more than made up for by the more rapid filtration due partly to the fine granular precipitate of calcium oxalate obtained and also to this not being contaminated by the flocculent alumina precipitate.

The oxalic acid method is just as accurate as the longer one of separating the silica, iron and alumina from the solution, before precipitating the lime. Indeed—unless the iron and alumina are separated by double precipitation it is the more accurate of the two.

A determination can be made by the above method in from twenty-five to thirty minutes, of which ten or fifteen are required for the lime to settle. The ammonia must not be added in very large excess and to guard against this the addition can best be made from the bottle shown in Fig. 130, on page 447.

DETERMINATION OF FERRIC OXIDE

By Titration with Potassium Permanganate. (Marguerite's Method)

Standard Potassium Permanganate

Dissolve 1.975 grams of pure crystallized potassium permanganate in 100 cc. of water, boil and allow to stand all night. In the morning filter through asbestos into a bottle and dilute to one liter. To test, or standardize, the solution, weigh into each of two beakers 0.4900 gram of pure ferrous ammonium sulphate, equivalent to 0.1 gram of ferric oxide, Fe_2O_3. Dissolve in 50 cc. of water, without heating, add 10 cc. of dilute sulphuric acid and run in the permanganate from a burette until the color of the solution

in the beaker just begins to turn pinkish. Take the reading of the burette and then add another drop, which should cause the solution to become decidedly pinkish. Divide the weight of ferric oxide (0.1 gram) equivalent to the weight of ferrous ammonium sulphate taken for the titration (0.49 gram) by the number of cubic centimeters of permanganate required; the result will give the ferric oxide equivalent to 1 cc. of the permanganate.

To use iron wire in standardizing, clean two pieces of fine iron wire, weighing 0.1 gram each, by rubbing first between emery paper and then with a cloth. Coil around a lead pencil and weigh each coil. Put 30 cc. of dilute sulphuric acid in a strong gas

Fig. 134.—Stopper and valve for iron reductions.

bottle provided with a perforated stopper through which passes a perfectly fitting glass tube with a hole blown in its side (Fig. 134). Heat the acid to boiling and drop in a coil of wire. When the solution of the latter is complete, remove the bottle from the source of heat and, after closing the opening by pushing the perforated glass tube down until its opening is closed by the stopper, allow the gas bottle to cool. When cold titrate the solution with the permanganate solution as above. Multiply the weight of the iron wire by 0.003 and deduct the result from the original weight for impurities. Multiply the corrected weight by 1.4286, or divide by 0.7, and divide by the number of cubic centimeters of permanganate required. The result will be the ferric oxide equivalent of 1 cc. of the standard potassium permanganate. Repeat the test with the other weighed coil of iron wire. The values for each cubic centimeter of permanganate by the two titrations should agree closely. Yet another way is to dissolve the iron wire in 15 cc. of dilute sulphuric acid in a beaker, cool, dilute, pass through the reductor, described on page 461, and titrate with the permanganate, calculating the results as above.

The Determination

The Committee on Uniformity in Analysis of Materials for the Portland Cement Industry, of the New York Section of the Society of Chemical Industry, recommend that the determination of ferric iron be conducted on the ignited precipitate of ferric oxide and alumina, after weighing, in the following manner:

The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 3 to 4 grams of $KHSO_4$, or, better, $NaHSO_4$, the melt taken up with so much dilute H_2SO_4 that there shall be no less than 5 grams absolute acid and enough water to effect solution on heating. The solution is then evaporated and eventually heated till acid fumes come off copiously. After cooling and redissolving in water the small amount of silica is filtered out, weighed, and corrected by HFl and H_2SO_4.[1] The filtrate is reduced by zinc, or preferably by hydrogen sulphide, boiling out the excess of the latter afterwards whilst passing CO_2 through the flask, and titrated with permanganate.[2] The strength of the permanganate solution should not be greater than 0.0040 gram Fe_2O_3 per cc.

The Committee appointed by the Lehigh Valley Section of the American Chemical Society direct also that the determination shall be carried out on the precipitate of oxide of iron and alumina. Their method differs from the above chiefly in the manner of reduction, and is as follows:

Add 4 grams acid potassium sulphate to the crucible containing the ignited oxides of iron and alumina, and fuse at a very low heat until oxides are wholly dissolved—twenty minutes at least; cool; place crucible and cover in small beaker with 50 cc. water; add 15 cc. dilute sulphuric acid (1:4); cover and digest at nearly boiling until melt is dissolved; remove crucible and cover, rinsing them carefully. Cool the solution and add 10 grams powdered C. P. zinc, No. 20. Let stand one hour, decant

[1] This correction of Al_2O_3 Fe_2O_3 for silica should not be made when the HFl correction of the main silica has been omitted, unless that silica was obtained by only one evaporation and filtration. After two evaporations and filtrations 1 to 2 mg. of SiO_2 are still to be found with the Al_2O_3 Fe_2O_3.

[2] In this way only is the influence of titanium to be avoided and a correct result obtained from iron.

the liquid into a larger beaker, washing the zinc twice by decantation, and titrate at once with permanganate. Calculate the Fe_2O_3 and determine the Al_2O_3 by difference. Test Zn, etc., by a blank and deduct.

NOTES

Ferrous salts are oxidized by potassium permanganate in solutions containing free acid to ferric salts according to the reaction,

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Potassium permanganate does not give trustworthy results in the presence of free hydrochloric acid.

If the permanganate is prepared as directed above it is not changed very rapidly, provided it is kept in a dark place. It is well to standardize it occasionally, however.

To reduce the iron with hydrogen sulphide, place the solution into a flask and add to the solution one-tenth its volume of sulphuric acid and 25 cc. of strong hydrogen sulphide water. Heat to boiling. Now stopper the flask with a rubber stopper having two perforations through which two tubes pass. One tube should reach nearly to the bottom of the flask and the other just inside the stopper. Boil the solution until all hydrogen sulphide is expelled, passing carbon dioxide through the flask all the while, bringing it in through the long tube and out through the short one. The expulsion of the hydrogen sulphide may be tested by holding a piece of filter-paper moistened with lead acetate or nitrate solution, in the escaping steam from the short tube. As long as any hydrogen sulphide is present the paper is blackened or browned. The solution must be cooled in a current of carbon dioxide before titration with permanganate.

In dissolving the oxides of iron and aluminum in potassium bisulphate, the operation should be conducted at a low temperature, so as not to drive off the excess acid in the salt. The contents of the crucible should therefore be just hot enough to keep them fluid. The fusion with bisulphate is tedious, however, and until recently the writer determined ferric oxide in cement by the following methods. It is simpler than the above schemes and has the advantage of allowing a sample of 1 to 2 grams to be used for the determinations:

Weigh 1 gram of finely ground cement into a beaker and add 15 cc. of hydrochloric acid. Heat for ten to fifteen minutes, add 200 cc. of water and heat to boiling. Add ammonia in slight but distinct excess, boil a few minutes, allow the precipitate to settle, filter, using the filter-pump if one is at hand, and wash two or three times with hot water. Place a clean flask under the funnel and redissolve the precipitate in a mixture of 15 cc. dilute sulphuric acid and 60 cc. water, made up in the beaker in which the precipitation was effected. Wash the filter and silica

free from iron with cold water, pass through the reductor, described below, and titrate the solution with permanganate. Multiply the number of the cubic centimeters of standard permanganate by the ferric oxide value of the permanganate and then by 100. Divide the result

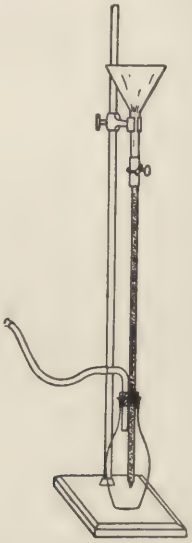


Fig. 135.—Shimer's reductor.

by the weight of cement taken; the quotient will be the per cent of ferric oxide, Fe_2O_3, in the cement.

The form of reductor best suited to cement work is the design of Dr. Porter W. Shimer, of Easton, Pa. His description of the apparatus[1] is as follows: "The reductor tube (*Fig.* 135) is a plain glass tube, three-eights inch internal diameter, drawn out and cut off at its lower end. It is filled by placing a few small pieces of broken glass in the drawn out portion, and on this about an inch of well cleaned sand. The tube is then filled with amalgamated zinc of as nearly uniform 20-mesh size as possible. About 80 grams are required. No asbestos or glass wool is used. The sand prevents particles of zinc from falling through and it does not become clogged by use. The consumption of zinc is very small, and when the column has settled about an inch a little fresh zinc can easily be poured in from above. The reductor tube is united with a 4-inch funnel by means of rubber tubing, well tightened with wire. Between the funnel and reductor is a Hoffman clamp. The lower end of the tube passes through a soft two-hole stopper so far as to reach

[1] *Jour. Amer. Chem. Soc.*, XXI, 723.

half way to the bottom of a heavy-walled pint gas bottle. The gas bottle is connected with a filter-pump through an intermediate safety bottle and valve. The funnel is clamped to a retort stand in such a manner as to allow the tube and gas bottle to swing easily in all directions. It is well to adjust the height so as to leave the gas bottle raised slightly above the base. The passage of the solution through the reductor may be effected either by use of the pump or by means of a vacuum obtained by condensation of steam devised originally in Bunsen's laboratory. In using the latter method a little water may be boiled in the gas bottle until all air is expelled, and then quickly unite with the reductor, the clamp on the filter-pump being closed. The speed of filtration is regulated by the upper clamp. Instead of filling the gas bottle with steam by boiling water in it, it is better to have a convenient tin or copper can containing boiling water and provided with one or more short steam outlet tubes on top. The empty gas bottle is inverted over one of these steam outlets and when filled with live steam, is taken off and united as quickly as possible with the reductor. This latter method has the advantage of starting with an empty gas bottle which is desirable on the score of accuracy."

To use the reductor, first pass, by the aid of suction, about 50 cc. of cold dilute sulphuric acid (1 part acid to 20 parts of water) through the reductor, and then follow with 200 cc. of cold distilled water. The Hoffman clamp should be closed before all the water has run out of the funnel so as to keep the tube full of water. Now empty the flask, again attach to the tube, pour the iron solution into the funnel and open the clamp. Just before the funnel becomes empty, run water around its sides and rinse the beaker well with water, running the washings also through the reductor, using about 100 to 150 cc. of water to wash the funnel and beaker. The time required for the iron solution to filter through the zinc, should be regulated by the upper clamp to occupy from three and a half to five minutes.

Instead of reducing the iron solution by means of a reductor, the gas bottle, mentioned on page 458, may be used. Pour the solution into the bottle. Add 1 gram of granulated zinc, stopper and allow to stand until the evolution of hydrogen slackens; then heat to boiling. When the zinc is completely dissolved (it may be necessary to add more acid to effect this), push down the glass tube, cool, and after adding 10 cc. of dilute sulphuric acid titrate with the permanganate.

The reduction may be accomplished with hydrogen sulphide also. The idea of the use of hydrogen sulphide is to do away with the error introduced by the presence of a small percentage of titanium, always found in cement. Titanium is reduced by zinc, and then oxidized by permanganate, causing the results for iron to be high. It is not reduced by hydrogen sulphide, hence the use of the latter. If the tita-

nium is not determined and deducted from the alumina, however, the latter is too high, by just so much, so that for practical purposes we might as well call titanium iron and use zinc as a reducing agent, as call it aluminum and use hydrogen sulphide.

By Titration with Potassium Bichromate. (Penny's Method)

Standard Potassium Bichromate

Weigh 3.074 grams of bichromate, dissolve in 250 to 300 cc. of cold water and pour into a liter graduated flask. Rinse out the beaker several times into the flask and dilute the solution to the liter mark. Mix well. One cc. of this solution should be equivalent to 0.005 gram of ferric oxide, Fe_2O_3.

To test or standardize the solution, weigh into a small beaker 0.4900 gram of pure ferrous ammonium sulphate (equivalent to 0.1 gram of ferric oxide). Dissolve in 50 cc. of water and, when all the salt is in solution, add 5 cc. of dilute hydrochloric acid. Run the bichromate solution from a burette into the liquid in the beaker until a drop of the iron solution placed upon a white porcelain plate and mixed by stirring with a drop of freshly made 1 per cent solution of potassium ferricyanide no longer assumes a blue color, but instead gives a yellow. This should require 20 cc. of the bichromate solution. If more or less, repeat the test, and if the first and second results agree, divide 0.1, the ferric oxide equivalent of the weight of the ferrous ammonium sulphate used, by the number of cubic centimeters of bichromate required. The result will give the ferric oxide equivalent, or value, in grams for each cubic centimeter of the standard potassium bichromate.

Some operators prefer to standardize their bichromate against iron wire. In this case clean 0.1 gram of fine iron wire by rubbing between fine emery paper and then between filter-paper. Coil around a lead pencil and weigh. Drop the coil in a small beaker, add 20 cc. of dilute hydrochlorirc acid and heat until all the wire dissolves. Wash down the sides of the beaker with a wash-bottle, bring the contents to a boil and drop in the stannous chloride solution, described below, slowly until the last drop turns the solution colorless. Remove from the source of heat and

cool the liquid rapidly by setting the dish in a vessel of cold water. When nearly cold add at once 15 cc. of saturated mercuric chloride solution, and stir well. Allow to stand a few minutes and titrate with the bichromate as described above. Multiply the weight of the iron wire by 0.003 and deduct this from the original weight, for the impurities in the wire. The corrected weight divided by 0.7 and then by the number of cubic centimeters of bichromate required, gives the ferric oxide equivalent in grams to each cubic centimeter of the standard bichromate. This value should be checked unless within limits of allowable error to 0.005 gram.

Stannous Chloride Solution

Dissolve 100 grams of stannous chloride in a mixture of 300 cc. of water and 100 cc. of hydrochloric acid. Add scraps of metallic tin and boil until the solution is clear and colorless. Keep this solution in a closely stoppered bottle (best a dropping battle) containing metallic tin. This solution should be kept from the air.

Mercuric Chloride Solution

Make a saturated solution of mercuric chloride by putting an excess of the salt in a bottle and filling up with water and shaking as the solution gets low.

The Determination

Weigh 1 gram of finely ground cement into a small beaker and add 15 cc. of dilute hydrochloric acid, heat from ten to fifteen minutes and add a little water. Heat to boiling and filter through a smaller filter, washing the residue well with water and catching the filtrate and washings in a porcelain dish. Add to the solution 5 cc. of dilute hydrochloric acid and bring to a boil. Add carefully, drop by drop, the stannous chloride solution until the last drop makes the solution colorless. Remove from the burner and cool the liquid by setting in a vessel of cold water. When nearly cold add 15 cc. of the mercuric chloride solution and stir the liquid in the dish with a glass rod. Allow the mixture to stand for a few minutes, during which time a slight white precipitate should form. Run in the standard bichromate solution

carefully from a burette until a drop of the iron solution tested with a drop of 1 per cent solution of potassium ferricyanide no longer shows a blue, but instead a yellow color. Multiply the number of cubic centimeters of bichromate used by the ferric oxide equivalent per cubic centimeter of the bichromate and divide the product by the weight of the sample. The result multiplied by 100 gives the per cent of the ferric oxide, Fe_2O_3, in the cement.

NOTES

Treatment with hydrochloric acid is sufficient to dissolve all except a mere trace of iron in Portland cement.

A strongly acid solution of ferric chloride, if boiling hot, is instantly reduced to ferrous chloride by a solution of stannous chloride according to the following reaction:

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

The operator can tell when complete reduction has taken place by the disappearance of the yellow color of the solution. The excess of stannous chloride is removed by addition of mercuric chloride when the following takes place:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

The precipitate, Hg_2Cl_2 should be white; if colored gray, too much stannous chloride was used in reduction and mercury has been formed. As mercury reacts with the bichromate, when the precipitate formed on adding mercuric chloride is not perfectly white, but is colored gray, the determination should be repeated using more care to avoid a large excess of the tin solution. If no precipitate is formed on addition of mercuric chloride the stannous chloride has not been added in excess, and all the iron will not have been reduced to the ferrous state.

Ferrous salts are oxidized to ferric compounds by bichromate when in a solution containing a considerable excess of hydrochloric or sulphuric acid. The reaction is:

$$6FeCl_2 + K_2CR_2O_7 + 14HCl = 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O.$$

The ferrous ammonium sulphate has the formula $Fe(NH_4)_2(SO_4)_2.6H_2O$. It, therefore contains one-seventh its weight of iron and is equivalent to 0.20408 of its weight of ferric oxide, Fe_2O_3. Fe_2O_3.

To make a 1 per cent solution of potassium ferricyanide dissolve 1 gram of the salt in 100 cc. of water. Ferric compounds give a yellow color to this solution, while ferrous compounds impart an intense blue color. This solution must always be made up fresh as it is reduced by exposure to light.

The writer has experimented considerably with the above, and he has found it thoroughly reliable. The presence of titanium does not affect its accuracy and a determination can easily be made in from fifteen to twenty minutes.

DETERMINATION OF SULPHURIC ANHYDRIDE

Gravimetric Method

Weigh 1 gram of the sample into a small dry beaker and stir it up with 5 cc. of cold water until all lumps are broken up and the lighter particles are in suspension. Add 5 cc. of concentrated hydrochloric acid and heat until solution is complete. Add 40 cc. of water. Filter through a small paper and wash the residue thoroughly. Dilute the filtrate to 250 cc., heat to boiling, and add 10 cc. of boiling 10 per cent barium chloride solution. Stir well and allow to digest on the steam bath until the precipitate has settled. If time is no object let the beaker stand over night. Filter,[1] ignite, and weigh as $BaSO_4$, which multiplied by 0.34300 gives SO_3.

Photometric Method

Jackson[2] has devised a rapid photometric method for determining sulphuric acid which is very convenient for checking this constituent in a large number of samples.

The apparatus used in this method is shown in Fig. 136. There is a glass tube closed at the bottom and graduated in millimeters depth. A convenient form of tube is a Nessler jar 2.5 centimeters in diameter and 17 centimeters to the 100 cc. mark. The brass holder for this tube is open at the bottom so that the glass tube rests on a narrow ring at this point. The candle below is so adjusted by means of a spring that the top edge is always just 3 inches below the bottom of the glass tube. The illustration shows the candle with the regulator cap removed so as to better represent the process. The English Standard Candle is preferred, but a common candle of the same size may be used. This candle must always be properly trimmed and the determination must be

[1] See page 472.

[2] *Chemical Engineer*, I., **6**, 361.

made rapidly so as not to heat the liquid to any extent. The most accurate work is obtained in the dark room, and the candle should

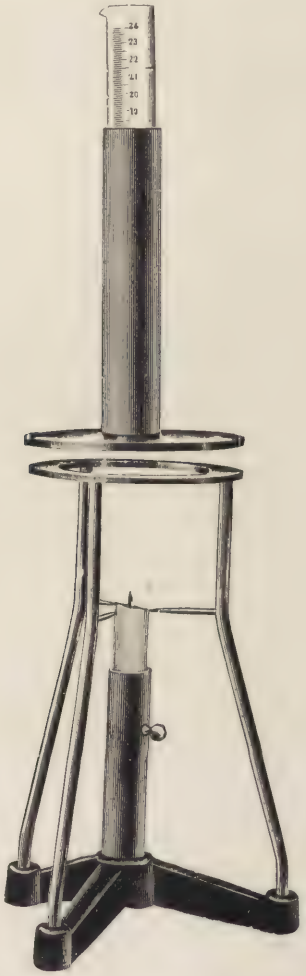


Fig. 136.—Jackson's apparatus for the photometric determination of sulphuric anhydride.

be so placed as not to be subjected to a draft of air. Care should be taken to keep the bottom of the tube clean both inside and out so as not to cut out any of the light.

To determine the sulphate in a cement weigh out 1 gram, correct to centigrams, and rub up thoroughly with a glass rod in a small porcelain dish, or casserole, with 2 cubic centimeters of strong hydrochloric acid. Add about 10 cubic centimeters of water and heat to boiling. Filter and wash with a small amount of hot water into a 100 cc. graduated Nessler jar, and fill with cold water nearly to the 100 cc. mark. If necessary suction may be employed in filtering, but usually a folded rib filter will do. Now add 2 grams of solid barium chloride crystals and make

TABLE XLII.—FOR THE DETERMINATION OF SULPHATE IN CEMENT

Depth cm.	Per cent SO_3	Depth cm.	Per cent SO_3	Depth cm.	Per cent SO_3	Depth cm.	Per cent SO_3
1.0	5.2	4.0	1.4	7.0	0.8	10.0	0.6
1.1	4.8	4.1	1.4	7.1	0.8	10.2	0.6
1.2	4.4	4.2	1.3	7.2	0.8	10.4	0.6
1.3	4.1	4.3	1.3	7.3	0.8	10.6	0.5
1.4	3.8	4.4	1.3	7.4	0.8	10.8	0.5
1.5	3.6	4.5	1.3	7.5	0.8	11.0	0.5
1.6	3.4	4.6	1.2	7.6	0.8	11.2	0.5
1.7	3.2	4.7	1.2	7.7	0.7	11.4	0.5
1.8	3.0	4.8	1.2	7.8	0.7	11.6	0.5
1.9	2.9	4.9	1.2	7.9	0.7	11.8	0.5
2.0	2.7	5.0	1.1	8.0	0.7	12.0	0.5
2.1	2.6	5.1	1.1	8.1	0.7	12.2	0.5
2.2	2.5	5.2	1.1	8.2	0.7	12.4	0.5
2.3	2.4	5.3	1.1	8.3	0.7	12.6	0.5
2.4	2.3	5.4	1.0	8.4	0.7	12.8	0.4
2.5	2.2	5.5	1.0	8.5	0.7	13.0	0.4
2.6	2.1	5.6	1.0	8.6	0.7	13.5	0.4
2.7	2.1	5.7	1.0	8.7	0.7	14.0	0.4
2.8	2.0	5.8	1.0	8.8	0.6	14.5	0.4
2.9	1.9	5.9	1.0	8.9	0.6	15.0	0.4
3.0	1.9	6.0	0.9	9.0	0.6	15.5	0.4
3.1	1.8	6.1	0.9	9.1	0.6	16.0	0.4
3.2	1.7	6.2	0.9	9.2	0.6	16.5	0.4
3.3	1.7	6.3	0.9	9.3	0.6	17.0	0.3
3.4	1.6	6.4	0.9	9.4	0.6	17.5	0.3
3.5	1.6	6.5	0.9	9.5	0.6	18.0	0.3
3.6	1.6	6.6	0.9	9.6	0.6	18.5	0.3
3.7	1.5	6.7	0.8	9.7	0.6	19.0	0.3
3.8	1.5	6.8	0.8	9.8	0.6	19.5	0.3
3.9	1.4	6.9	0.8	9.9	0.6	20.0	0.3

up to the 100 cc. mark with cold distilled water. Pour back and forth from the tube to a beaker until all of the barium chloride is dissolved. The solution is now ready for examination.

The candle is trimmed and lighted; the solution is poured back and forth to get a thorough mixture of the precipitate of barium sulphate; and the glass tube is placed in position in the holder. The liquid containing the precipitate is now poured into a graduated tube until the sight of the image of the flame of the candle is just visible. Then pour in a few drops at a time until it just disappears from view. The height to which this solution stands in the tube (reading the bottom of the meniscus) is then taken and from this reading the percentage of sulphates present in the cement may be read directly from Table XLII.

DETERMINATION OF TOTAL SULPHUR

By Solution in HCl and Br

Weigh 1 gram of the sample into a dry beaker and stir it up with 30 cc. of bromine water until all lumps are broken up and all except the heavier particles are in suspension. Add 15 cc. of dilute hydrochloric acid (1 : 1) and heat until solution is complete. Filter off the residue through a small filter and wash thoroughly with hot water. Dilute to 250 cc. and boil until all bromine is expelled. Now to the boiling solution add 10 cc. of 10 per cent barium chloride solution, also boiling, and proceed as in the determination of sulphates.

By Fusion With Na_2CO_3 and KNO_3

Place 1 gram of cement, finely ground and dried, in a large platinum crucible and thoroughly mix it by stirring with 6 grams of sodium carbonate and a little sodium or potassium nitrate.

Fuse the mixture, being careful to avoid contamination from sulphur in the gases from source of heat. This may be done by fitting the crucible in a hole in an asbestos board. The heating of the crucible should be gradually done first over a Bunsen burner for awhile and then over a blast-lamp, until the contents of the crucible are in quiet fusion. Run the fused mass well up on the sides of the crucible and chill by dipping the bottom of the crucible in a vessel of cold water. If loose, remove the mass from the crucible to a beaker and cover with hot water. If not loose,

fill the crucible with hot water and digest until the mass breaks up; then remove to the beaker. Cover the latter with a watch-glass and acidify with hydrochloric acid. When effervescence ceases remove the watch-glass, rinse into the dish and filter. Dilute the filtrate to 250 cc. and heat to boiling. Add 10 cc. of 10 per cent barium chloride solution, also heated to boiling. Stir and heat for a few minutes and proceed as in the determination of sulphates.

DETERMINATION OF SULPHUR PRESENT AS CALCIUM SULPHIDE

Weigh 5 grams of cement into a porcelain dish, and titrate with water until it shows no further tendency to set. Then wash out into the flask (Fig. 137) and cork tightly. Two-thirds fill the 10-inch test-tube with a solution of lead oxide in caustic potash made by adding lead nitrate solution to potassium hydroxide so-

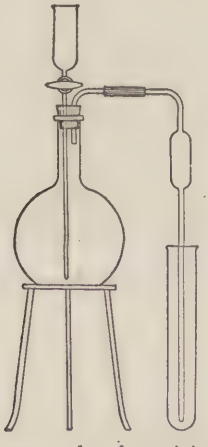


Fig. 137.—Apparatus for determining sulphides.

lution (sp. gr. 1.27) until a permanent precipitate forms, and then filtering off the solution through asbestos after allowing the precipitate to settle. Run into the flask by means of the funnel 50 cc. of dilute hydrochloric acid and apply heat gently. Finally

bring the acid to a boil and disconnect the delivery tube from the flask at the rubber joint. Collect the precipitate on a small filter, wash it once with water and then while still moist throw the precipitate and filter back into the test-tube, in which has been placed some powdered potassium chlorate. Pour upon the filter and precipitate 10 cc. of concentrated hydrochloric acid. Allow to stand in a cool place until the fumes have passed off, then add 25 cc. of hot water, filter off the pulp, etc., and wash with hot water. Heat the filtrate to boiling and add ammonia until the solution is slightly alkaline. Then acidulate with a few drops of hydrochloric acid, add 10 cc. of a 10 per cent solution of barium chloride, also brought to a boil, boil for a few minutes and stand in a cool place over night. Filter, wash, ignite, and weigh as barium sulphate. Multiply this weight by 0.30895 for calcium sulphide, CaS, or by 0.13738 for sulphur, S.

NOTES

Instead of alkaline lead nitrate solution a solution of cadmium chloride made slightly alkaline with ammonia may be used to absorb the evolved hydrogen sulphide, in which case the cadmium sulphide precipitated, may be collected upon a previously weighed filter-paper, dried, weighed and the sulphur calculated from this weight. For this method use 10 grams of cement for the sample and fill the test-tube two-thirds full of a solution of cadmium chloride, made by dissolving 3 grams of cadmium chloride in 75 cc. of water, adding ammonia until the precipitate at first formed redissolves and then diluting to 500 cc. Proceed as usual. Collect the precipitate of cadmium sulphide upon a small counterpoised filter, or better in a Gooch crucible and felt, wash with water to which a little ammonia has been added, dry at 100° C., and weigh as cadmium sulphide, CdS. The weight of cadmium sulphide multiplied by 0.5000 gives the equivalent amount of calcium sulphide. Calculate the percentage and report as such or merely report as sulphur. If the former, calculate the total sulphur, as found by either of the methods on page 469 to calcium sulphate, by multiplying the weight of the barium sulphate by 0.58327. Now multiply the percentage of calcium sulphate so found by 0.41195 and deduct the product from the percentage of lime (as found by precipitation as oxalate in the general scheme). The difference should be reported as calcium oxide, or lime, CaO. Multiply the percentage of calcium sulphide by 1.8872 for its equivalent in calcium sulphate and deduct from the percentage of total sulphur calculated as calcium sulphate. Report the difference as calcium sulphate.

Calcium sulphide may also be determined indirectly by determining first the sulphur present as sulphate and then the total sulphur. The difference will represent the sulphur present as sulphide. This may be reported either as CaS or as S. By this method, however, errors are made to appear as CaS.

Barium sulphate is a troublesome precipitate to filter as it is likely to run through the paper. For this reason it is well to use a double paper. Some operators use a Gooch[1] crucible, but a device suggested by Dr. Porter W. Shimer, of Easton, Pa., is still handier. It is shown in its simplest form in Fig. 138.[2] It consists of a glass tube cut off square at both ends, 2 inches long and 1 inch in internal diameter.

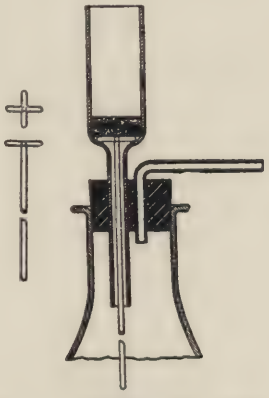


Fig. 138.—Shimer's filter tube.

The edges should be left sharp and not rounded in the flame. In the bottom of the tube is a rubber stopper fitted with a glass tube for attachment to the suction flask. On the stopper when inserted into the tube is a disk of piano felt three-sixteenths inch thick, fitting closely into the tube. The filter tube is now ready for the filter. Take unwashed Swedish filter-paper, in any convenient amount, crush it into a ball in the hand and place it in a large cerecene hydrofluoric acid bottle from which the upper part has been cut. Add hydrochloric acid (sp. gr. 1.12 to 1.18) and a little hydrofluoric acid and stir vigorously with a paraffin-coated wooden stirrer until the paper has become a mass of fine soft pulp. Let it stand a few minutes and then add distilled water. In preparing a filter, pour some of this pulp in the beaker, dilute further with distilled water and pour enough on the felt, under suction, to make a filter of about one-fourth inch. Compact this well by hard stamping with a stamper made from a solid rubber stopper, the larger end of which is only

[1] See page 450.

[2] *Jour. Amer. Chem. Soc.*, XXVII, 287. *Chemical Engineer*, II, 39.

a little smaller than the inner diameter of the tube. A hole is made in the small end of the stopper, but not deep enough to pass quite through and a short glass rod inserted in this for a handle. Wash the filter two or three times with water and then filter off and wash the barium sulphate, using suction. This may be done rapidly without fear of a trace of the precipitate getting into the filtrate.

When filtration and washing are complete, turn off the suction and remove the filter tube from the stopper. Take the stamper and push the felt up until the filter projects beyond the tube, when the filter may be detached from the felt by a pair of forceps, or, if preferred, the upper end of the tube may be inserted into the weighed crucible and the felt and filter may be pushed at once into it, when the felt can be readily removed and the precipitate and filter ignited. Any precipitate adhering to the sides of the tube is taken along by the outgoing filter, for this reason the tube should be of uniform diameter, etc. The ash of these filters is less than that of an ordinary filter and the apparatus gives excellent results. It may, of course, be used for making other filtrations, but is particularly well adapted for use with barium sulphate.

It now seems to be pretty well established that it is not necessary to evaporate to dryness and separate silica, before precipitating sulphur with barium chloride, provided the solution is sufficiently dilute to guard against separation of gelatinous silica.

LOSS ON IGNITION

Weigh 1 gram of cement into a weighed platinum crucible, cover with a lid, and heat for five minutes over a Bunsen burner, placed as directed below, starting with a low flame and gradually raising it to its full height. Then heat for fifteen minutes over a blast-lamp. Cool and weigh. The loss of weight represents the loss on ignition.

In conducting the ignition the crucible should be placed with its bottom projecting through a round hole in a piece of platinum foil, which in turn rests upon a piece of asbestos board with a slightly larger hole cut in it. The flame should be played at an angle upon the bottom of the crucible so that the products of combustion are swept away from it.

This loss consists mainly of combined water and carbon dioxide driven off by the high temperature. Some chemists report, therefore, as "carbon dioxide and water," or having found the carbon dioxide subtract the percentage from that of the "loss on igni-

tion" and call the remainder "water of combination" or combined water. As both sulphuric acid and alkalies are driven off, to some extent, at the temperature of the blast-lamp, this is not strictly correct and it is best to merely report as "loss on ignition." This loss of alkalies is shown by the fact that if the crucible lid is rinsed off with distilled water, after the crucible has been ignited and weighed, and is then ignited for a moment to dry it and placed back on the crucible, the weight of the whole will be from 0.5 milligram to 1.5 milligrams lighter, showing the condensation of the alkalies on the lid.

A PHOTOMETRIC METHOD FOR MAGNESIA IN PORTLAND CEMENT

Mr. W. E. Haskell, mix chemist, Old Mission Portland Cement Co., has devised a photometric method for determining magnesia in cement.[1] He employs the Jackson photometer described on page 466. The tube of his apparatus was 27 mm. internal diameter and graduated in millimeters to the 25 cm. mark. The top edge of the candle holder was 4 inches below the bottom of the glass tube instead of three inches as is usual for sulphur.

In employing this method, the analysis of the cement is conducted in the usual manner, including the precipitation of the lime. The filtrate from the lime is made slightly acid and evaporated to about 200 cc. and is then neutralized with ammonium hydroxide, using methyl orange as an indicator, cooled to 15 degrees Centigrade and diluted to 250 cc.

This solution is then transferred to the 600 cc. beaker in which the evaporation was made, treated with 40 cc. of a saturated solution of sodium ammonium hydrogen phosphate, the volumetric flask rinsed out with 25 cc. concentrated ammonium hydroxide and the latter added to the solution in the beaker. (These quantities should be fairly exact).

The solution is then stirred vigorously for two minutes with a stirring rod to which a broom shaped policeman, three centimeters wide, is fastened. The stirring is done across the diameter of the beaker, avoiding a circular motion of the rod, and the

[1] Private communication to the author.

rubber policeman rubbed energetically along the bottom of the beaker. A fine granular precipitate is thus produced.

The solution, without being allowed to settle, is poured into the photometer tube until the image of the candle flame is just obscured. The weight of magnesium oxide corresponding to the reading on the tube is then obtained from Table LXIII. The small amount in the photometer tube is transferred back into the beaker and the stirring repeated for two minutes more and a reading again taken. This last reading should be taken as final.

Where the percentage of magnesia is higher than 3 per cent it is necessary to use an aliquot portion of the solution.

TABLE LXIII.—For the Photometric Determination of Magnesia in Cement

Tube Readings mm.	Miligrams of MgO				
	0.0 mm.	0.2 mm.	0.4 mm.	0.6 mm.	0.8 mm.
3	17.5	16.8	16.1	15.4	14.7
4	12.9	12.2	11.5	10.8	10.1
5	9.4	9.1	8.8	8.5	8.2
6	7.9	7.7	7.5	7.3	7.1
7	6.9	6.7	6.6	6.4	6.3
8	6.1	6.0	5.9	5.7	5.6
9	5.5	5.4	5.3	5.2	5.1
10	5.0	4.9	4.8	4.8	4.7
11	4.6	4.5	4.4	4.4	4.3
12	4.2	4.1	4.0	4.0	3.9
13	3.8	3.7	3.7	3.6	3.6
14	3.5	3.5	3.4	3.4	3.3
15	3.3	3.3	3.2	3.2	3.1
16	3.1	3.1	3.0	3.0	2.9
17	2.9	2.9	2.8	2.8	2.7
18	2.7	2.7	2.6	2.6	2.5
19	2.5	2.5	2.4	2.4	2.3
20	2.3	2.3	2.2	2.2	2.2

DETERMINATION OF CARBON DIOXIDE AND COMBINED WATER

Apparatus

For carrying out the determination of carbon dioxide and combined water at the same time, the apparatus designed by Dr. Porter W. Shimer, of Easton, Pa., for carbon combustions is best suited.

The apparatus as used for carbon dioxide and combined water determinations is illustrated in Fig. 139. It consists of the following parts:

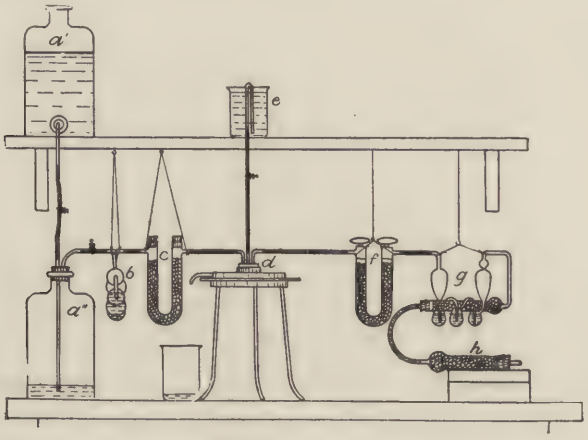


Fig. 139.—Apparatus for determining carbon dioxide and water with Shimer's crucible.

1. The aspirator bottles, *a'* and *a''*, the upper *a'*, filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.

2. A potash bulb, *b*, containing a solution of caustic potash of 1.27 sp. gr. The form of bulb shown in the cut is Liebig's. Mohr's or any other form will do as well, but the Leibig bulb is the cheapest and answers as well here as the more expensive forms.

3. A U-tube, *c*, filled with dried granular calcium chloride. A straight calcium chloride tube may be used in place of the U-tube. It takes up more room, however.

4. A platinum crucible, *d*, provided with a water-jacketed stopper and reservoir, *e*, for supplying water to this latter. Fig. 140 shows the crucible stopper, etc., in detail. The water-cooled stopper is made of German silver and is ground into the crucible. This joint may easily be kept tight by an occasional grinding in, using for this purpose a little glass finely ground with oil. The crucible is of 60-cc. capacity, deep in form and weighs about 50

grams. The crucible is accurately fitted with a knurled ring around the upper part, this ring is easily removed. The crucible rests with its bottom through a circular opening in a piece of

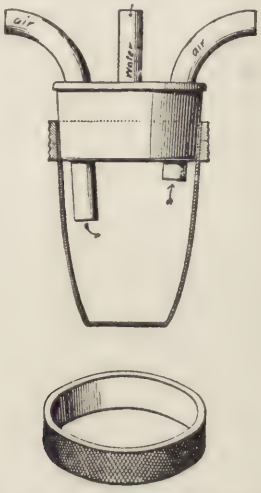


Fig. 140.—Shimer's water-jacketed crucible.

three-sixteenths inch asbestos board which in turn rests upon a tripod.

5. A small **U**-tube, *f*, filled with dried granular calcium chloride. The best form is that shown, provided with arms and glass stopcocks.

6. A potash bulb, *g*, with calcium chloride tube attached. The bulb should be filled with caustic potash of 1.27 specific gravity, and the tube with dried granular calcium chloride.

7. A guard tube, *h*, filled with dried granular calcium chloride.

Testing the Apparatus

Fill the reservoir, *e*, with boiling water. Half fill the crucible with freshly ignited asbestos, and close it with the water-cooled stopper. See that the apparatus is perfectly tight by running the aspirator and pinching the tube together just after the potash bulb.

Open the clamp and allow water to run out of the stopper. Place a Bunsen burner under the crucible. Open the clamp be-

tween the lower aspirator bottle and the potash bulb, *b*, and aspirate a current of air through the apparatus slowly for about twenty minutes. Detach the potash bulb, *g*, and the calcium chloride tube *f*, and weigh. Again connect the bulb and tube in the train and aspirate air slowly through the apparatus for another twenty minutes. Detach the bulb, *g*, and tube, *f*, and again weigh them. This weight should agree to within 0.0005 of the former weight for the potash bulb, and 0.0003 for the calcium chloride tube. If not, after making sure there is no leakage in the apparatus, repeat the test. When the weights agree within the limits given, take the last pair as the weights of the bulb and tube, and proceed with the determination.

The Determination

Weigh into the crucible from 1 to 3 grams of cement, cover with ignited asbestos and stopper tightly. Test the apparatus and be sure there is no leakage. Place the Bunsen burner under the crucible after starting the hot water to flowing through the stopper. Cause a slow current of air from the aspirator bottle to flow through the apparatus. After ten minutes replace the Bunsen burner by a blast-lamp and continue the ignition for twenty minutes. Remove the lamp and aspirate air through the apparatus for ten minutes longer. Detach the potash bulb, *g*, and the calcium chloride tube, *f*, and weigh. The increase in weight of the former represents the carbon dioxide, CO_2, and of the latter water, H_2O.

NOTES

In this method the combined water and the carbon dioxide are driven out of the cement by ignition; the former is absorbed in a weighed calcium chloride tube and the latter in a weighed potash bulb. The increase in weight of the tube and bulb respectively represent the weight of combined water and carbon dioxide in the cement sample. The air entering the apparatus for the purpose of aspiration is purified of any water and carbon dioxide it is sure to contain by passing through the caustic potash and then over calcium chloride.

To make the upper aspirator bottle, bore a hole near the bottom of a five-pint bottle with a file dipped in turpentine and then slip into this hole a bit of glass tube covered with an inch or so of soft, thick-walled rubber tubing.

To fill the potash bulbs attach a short piece of rubber tubing to one end and dipping the other end in the caustic potash solution contained in a shallow dish apply suction to the rubber tubing with the mouth. When the bulbs are filled to the proper height (See Fig. 139) wipe the end dry inside and outside with pieces of filter-paper.

Instead of the bulb, *b*, the air may be purified of any carbon dioxide it contains by causing it to bubble through caustic potash solution contained in two four-ounce wide-mouthed bottles.

Calcium chloride sometimes, though not often, contains calcium oxide, which would absorb carbon dioxide. To saturate this, connect the apparatus, leaving out the potash bulb, *f*, and place a small piece of marble in the crucible. Now heat the crucible with a blast-lamp and aspirate air slowly through the apparatus. Then take the marble out of the crucible and aspirate air for twenty minutes longer.

The potash bulbs and **U**-tube should be weighed as follows: Place the bulb upon one balance pan, and on the other the approximate weight. Stand the **U**-tube in the balance case. Close the door and do not open it for exactly twelve minutes. Then finish weighing the bulb so that

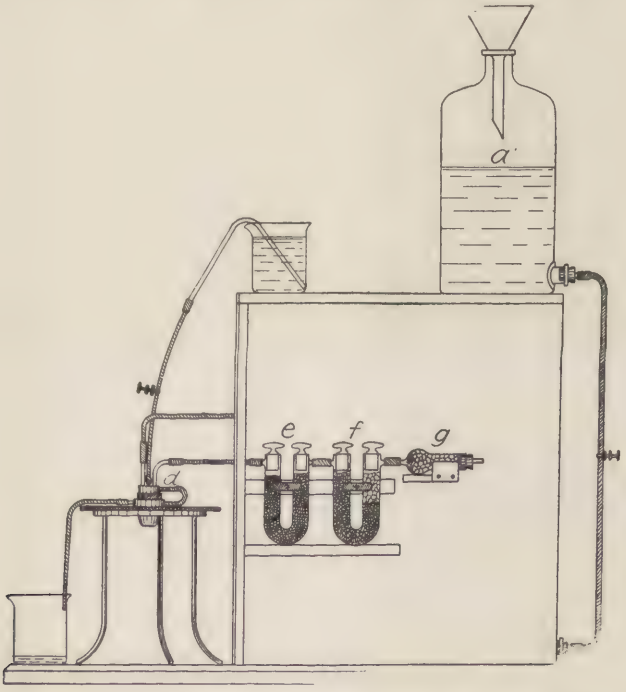


Fig. 141.—Portable apparatus for carbon dioxide and water. Front.

the exact result is obtained in fifteen minutes from the time the bulb was placed on the pan. Now remove the bulb and weigh the **U**-tube quickly.

When not attached in the train the **U**-tube should have its stop-cocks turned so as to close the openings and the potash bulb should be "capped" with short pieces of rubber tubing containing, in one end, bits of capillary glass tubing.

If the cement should contain any appreciable quantity of carbonaceous matter, such as unburned coke, this would be burned to carbon dioxide causing high results. In this case first determine the carbon dioxide given off on ignition. Then weigh another sample into the crucible, add a little hydrochloric acid, filter off the residue on ignited

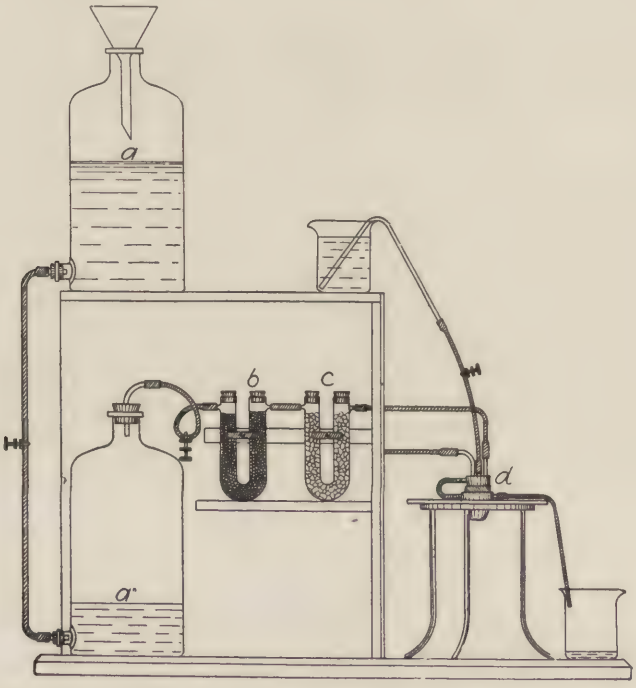


Fig. 142.—Portable apparatus for carbon dioxide and water. Back.

asbestos, dry at 100° C., and determine the carbon dioxide in the residue as before. This will represent the carbon dioxide due to the burning of the organic matter. The difference, of course, represents the carbon dioxide present in the cement as carbonate.

A **U**-tube, containing soda-lime, may replace the potash bulb, *g*. This tube should be similar to *f*, and provided with ground glass stoppers. About an inch of calcium chloride should top the soda-lime in the limb next the guard tube, *h*.

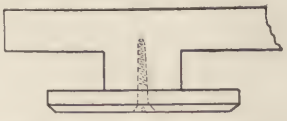


Fig. 143.—Clamp for U-tubes.

When many carbon dioxide determinations have to be made, it will be found convenient to arrange the apparatus on a stand as shown in Figs. 141 and 142. Fig. 141 shows the front of the apparatus and Fig. 142 the reverse. The stand consists of a wooden base 1½ inches thick, and upon this is mounted an upright board. At the end of this board and running entirely across the base is fastened another upright at right angles to the first. These uprights support a shelf upon which rests the upper aspirator bottle and the reservoir for the water-cooled stopper. The upright nearest the tripod should be protected against the heat of the blast lamp by covering with a sheet of asbestos. The **U**-tubes, etc., rest upon shelves as shown. The manner of clamping the **U**-tubes to the board is also shown in Fig. 143. *a'* and *a''* (Fig. 142) are aspirator bottles; *b* is filled with soda-lime and *c* with calcium chloride; *d* is Shimer's special form of water-jacketed platinum crucible; *e* (Fig. 141) is filled with calcium chloride, *f* with soda-lime topped with calcium chloride, and *g* with calcium chloride.

DETERMINATION OF CARBON DIOXIDE ALONE

The apparatus just described for carbon dioxide and combined water determinations may, of course, be used for determining carbon dioxide only. In this case it is not necessary to weigh the calcium chloride tube, *f*, and in place of the expensive **U**-tube with its ground glass stop-cocks, a simple straight form calcium chloride tube can be used just as well. Neither is it necessary to supply the stopper with hot water, and an empty potash bulb can replace the calcium chloride tube *c*. The determination is carried out precisely as if both the water and carbon dioxide were being considered, with, of course, the exception of not weighing the tube, *f*, at the end of the operation. If the stopper is wet with the finger before insertion into the crucible, it will be found to go in easier. This is, of course, not permissible when the water also is determined.

Some chemists prefer to determine carbon dioxide by liberating this constituent with hydrochloric acid and absorbing the evolved gas in a weighed potash bulb.

For carrying out the determination refer to the apparatus (Fig. 139), for determining carbon dioxide and combined water. Omit the U-tube, *c*, and substitute for the crucible, *d*, a 100 cc. wide-mouthed flask provided with a funnel tube. Follow the

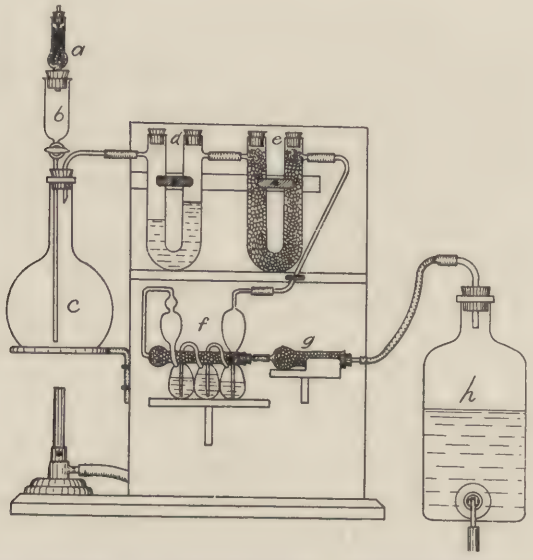


Fig. 144.—Apparatus for determining carbon dioxide by evolution method.

flask with a U-tube, containing sulphuric acid (sp. gr. 1.84) and this by the U-tube, *f*, the potash bulb, *g*, and the guard tube, *h*.

A convenient way of arranging the apparatus is shown in Fig. 144. *a* is filled with soda-lime; *b* is a funnel tube with ground glass stop-cock; *c* the 100-cc. flask; *d* contains sulphuric acid; *e* and *g* calcium chloride; *f* is the weighed potash bulb, and *h* the aspirator bottle.

The Determination

Weigh into the flask, *c*, from 2 to 4 grams of cement, titrate with water until all tendency to set has ceased, and connect

the soda-lime tube *a* with the funnel tube. Aspirate a few liters of air through the apparatus, disconnect and weigh the potash bulb with attached calcium chloride tube. Again connect the apparatus, aspirate another two liters, and again weigh the potash bulb and attached calcium chloride tube. If the first and second weights agree to within 0.0005 gram of each other, run into the flask 50 cc. of dilute hydrochloric acid and, if sulphides are present, mix with this a very little chromic acid. After connecting the bulb and tube in the train, and when action ceases apply heat gradually until the contents of the flask boil. Connect the soda-lime tube *a* and aspirate air slowly through the apparatus. Turn out the burner and aspirate two liters more of air. Disconnect the potash bulb and calcium chloride tube and weigh. The gain in weight is carbon dioxide. Divide the increase by the weight of the sample used and multiply the quotient by 100, for the percentage of carbon dioxide in the cement.

RAPID DETERMINATION OF CARBON DIOXIDE

The Apparatus

Where a determination of carbon dioxide has to be made only at rare intervals and where great accuracy is not essential, the Schrötter apparatus will be found convenient. It is shown in Fig. 145 and is made of blown glass. It consists of a decom-

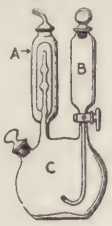


Fig. 145.

position flask, C; two reservoirs, A and B, communicating with it and a stoppered opening through which the sample is introduced into the flask.

The Determination

Weigh accurately 1 gram of the cement sample and introduce into the flask, C, through the opening. Stopper the latter. Fill the reservoir, B, with dilute (1 : 1) hydrochloric acid and half fill the second reservoir, A, with concentrated sulphuric acid. This latter is intended to dry the carbon dioxide as it leaves the apparatus. Now accurately weigh the apparatus. Allow the hydrochloric acid to flow gradually from the reservoir, B, into the flask by turning the stop-cock and removing the stopper of the reservoir, B, (not that of the flask). As soon as the reservoir is empty replace its stopper. Now place the apparatus on a wire gauze or hot-plate and heat the contents until it just boils. Open the stop-cock and remove its stopper, B, and attach an

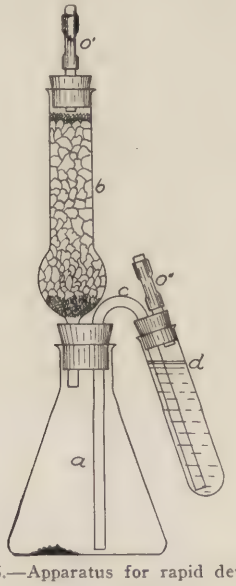


Fig. 146.—Apparatus for rapid determination of carbon dioxide.

aspirator to the opening of A. Draw a slow current of air through the apparatus until about 200 cc. of air have been drawn through. Disconnect the aspirator and allow the apparatus to cool. Stopper and weigh. The loss in weight represents the carbon dioxide.

The following apparatus which is a modification of Rose's form, may be made from material found in almost any laboratory. It is not so convenient, however, as the above apparatus. It consists (Fig. 146) of a small 50 cc. Erlenmeyer flask, *a*, provided with a two-hole rubber stopper. Through one hole of this latter passed a 3-inch calcium chloride tube, *b*, and through the other a piece of bent glass tubing, *c*, one arm of which reaches nearly to the bottom of the flask, the other through another stopper to the bottom of a small wide tube, *d*. This latter is made from a 5-inch test-tube. Such an apparatus will weigh from 35 to 60 grams according to the skill and choice of materials with which it is made.

Place a little wool or cotton in the bottom of the calcium chloride tube and then fill the tube with calcium chloride. Next two-thirds fill the tube, *d*, with dilute hydrochloric acid, and weigh into the flask from 2 to 3 grams of Portland cement. Moisten the cement thoroughly with water, place the stopper in the flask, cap the openings, *o'* and *o''*, with pieces of rubber tubing closed at one end with bits of glass rod, and set in the balance case. After ten minutes weigh. Now attach a small guard tube, filled with calcium chloride, to the opening, *o'*, and after uncapping, *o''*, suck the acid from the tube, *d*, into the flask, *a*. As soon as the acid is all in *a*, close *o''* with the finger and cap quickly. After effervescence ceases, uncap *a''*, attach the guard tube to this opening this time, uncap *o'* and blow air gently through the apparatus for five to seven minutes. Cap the openings, place in the balance case, and after ten minutes weigh. Always, before weighing, uncap either *o'* or *o''* for a few seconds and then recap. This allows the pressure, caused by the change of temperature, to adjust itself. The loss in weight represents the carbon dioxide, CO_2, in the cement. Divide the loss by the weight of the sample and multiply the result by 100 for the percentage.

DETERMINATION OF HYGROSCOPIC WATER

Weigh 5 grams of the sample upon a tared watch-glass, spreading the former over the latter in a thin layer and dry for one hour, (or until it ceases to lose weight) at a temperature of 100°-110° C. Cool in a desiccator and weigh. The loss in weight represents "Hygroscopic Water" or "water below 110° C." or "H_2O—110°."

NOTES

Instead of a watch-glass a weighed platinum or porcelain crucible or a weighing bottle may be used and a smaller sample (1 gram) taken.

DETERMINATION OF ALKALIES

J. Lawrence Smith's Method

Ammonium Chloride Solution: Dissolve 50 grams of ammonium chloride in 250 cc. of distilled water, place in a reagent bottle and add some potassium platinic chloride in excess (one or two precipitates from former determinations will do) and shake well. Allow to stand with frequent shakings for eight to twelve hours, settle over night and filter into another reagent bottle—decanting off from the heavy potassium platinic chloride precipitate.

Platinic Chloride: When made from recovered platinum each 100 cc. of solution should contain 2.07 grams of metallic platinum or 1 cc. = 0.01 gram K_2O (see recovery of platinum below).

Method for Total Potash in Cement, Raw Materials, Clinker, Stack Dust, Etc.

For ground raw mix and clinker use 4 grams of the sample, 1 gram of ammonium chloride and 4 grams of pure precipitated calcium carbonate (B. & A. or J. T. B Co.).

For clay, shale and feldspar use 1 gram of *very finely* ground sample, 1 gram of ammonium chloride and 8 grams of pure precipitated calcium carbonate.

For treater dust, stack crusts, etc. use ½ to 1 gram of dust, ½ gram of ammonium chloride and 4 grams of calcium carbonate.

Mix the finely ground substance with the ammonium chloride by grinding together in a clean agate mortar Add the calcium carbonate and transfer the mixture to a large platinum crucible provided with a closely fitting cover. The bottom of the crucible should have a layer of calcium carbonate spread over it Set a small platinum dish full of cold water on the cover to act as a cooler and condense any alkalies volatilized. Heat gently at first, then gradually raise the temperature to a full red heat and keep so for an hour. Cool the crucible and transfer the sintered mass to a porcelain or better a platinum dish. Wash the crucible and lid with hot water and pour into the dish. Digest the contents of the dish until the sintered mass slakes to a fine powder. If the sintered mass is not easily detached from the

crucible, put the crucible into the dish, add water, and heat until the mass slakes. Remove the crucible and wash off into the dish. Add 1.5 grams of pure ammonium carbonate, evaporate carefully to about 100 cc. and add a little more ammonium carbonate and a few drops of ammonia. Filter through a small filter into a dish. Test the filtrate with a few drops of ammonium carbonate solution to make sure all the calcium has been precipitated. If potash only is to be determined proceed as in *A*. If both potash and soda are to be determined proceed as in *B*.

A. To the filtrate from the ammonium carbonate precipitation add two or three drops of 1 : 1 sulphuric acid. Evaporate to dryness, dry in an air-bath for one-half hour and ignite at a red heat until all ammonium chloride is expelled and white fumes cease to come off. Cool, dissolve in a little water. The contents of the dish should be white and soluble without residue. Add to the solution a few drops of hydrochloric acid and an excess of platinic chloride. Evaporate nearly to dryness on the water-bath and add 20 cc. of 80 per cent alcohol. Let stand until the sodium salts dissolve. Filter through a weighed Gooch crucible with asbestos felt (which has been previously washed with acid, water and alcohol (80 per cent), and dried at 130° C). Keep the precipitate in the dish and wash with 80 per cent alcohol by decantation four or five times until the washings are colorless pouring the washings through the filter. Now wash the contents of the dish four or five times with the ammonium chloride solution. Transfer the precipitate to the filter with 80 per cent alcohol and wash five times with 80 per cent alcohol. Rinse off the outside of the crucible with alcohol, dry at 130° C. and weigh as potassium platinic chloride K_2PtCl_6.

$$\text{Potassium oxide} = K_2PtCl_6 \times 0.1938$$
$$\text{Potassium chloride} = K_2PtCl_6 \times 0.3067$$

B. Evaporate the filtrate from the ammonium carbonate precipitation to dryness and ignite at a barely visible red until all the ammonia salts are expelled and white fumes cease to come off. Cool, dissolve in a little water, add a few drops of barium chloride solution, and then a little ammonium carbonate and ammonium oxalate solution and ammonia, and filter from any

residue that may form. Add three or four drops of dilute hydrochloric acid to the filtrate and evaporate to dryness in a weighed platinum dish. Ignite carefully as before and weigh as sodium and potassium chloride, NaCl + KCl. Dissolve the mixed chloride in water and precipitate the potassium with platinic chloride, wash with 80 per cent alcohol (washing with ammonium chloride solution is unnecessary), dry and weigh as directed in *A*.

$$\text{Potassium oxide} = K_2PtCl_6 \times 0.1938,$$
$$\text{Sodium oxide} = (NaCl - K_2PtCl_6 \times 0.3067)\ 0.5303.$$

Method for Water-Soluble Potash in Treater Dust, Stack Crusts, Etc.

Boil 10 grams of the dust with 300 cc. of water for thirty minutes. Add to the hot solution a slight excess of ammonia and sufficient ammonium oxalate to precipitate all of the lime. Wash into a 500 cc. graduated flask, cool, dilute to the mark with water, mix well and pass some through a *dry* filter into a *dry* beaker. Measure 25 to 50 cc. of the filtrate with a pipette and run into a platinum dish. Evaporate to 5 to 10 cc. add two or three drops of sulphuric acid . Evaporate to dryness, heat in an air-bath one-half hour and proceed as directed above.

NOTES

Save all filtrates, washings and precipitates containing platinum. Dissolve the precipitates in hot water and add to the washings. Add metallic zinc (mossy) and dilute hydrochloric acid. Continue to add these as action ceases until all platinum is precipitated. Add acid in excess and when all zinc is dissolved, collect the platinum in a filter-paper. Wash well with hot water and hydrochloric acid alternately then finish washing with water. Ignite to destroy carbon and weigh. Treat with sufficient aqua regia to effect solution in a covered porcelain dish. Evaporate almost to dryness several times with strong hydrochloric acid to expel nitric acid. Dilute with water and filter (48 cc. of solution to each gram of platinum gives a solution 10 cc. = 0.1 gram K_2O).

During the first part of the incineration of the mixture of cement, calcium carbonate and ammonium chloride the heat should be kept low. The idea is not to volatilize the ammonium chloride, but to dissociate this into ammonia and hydrochloric acid by the heat. The latter then unites with the calcium carbonate to form calcium chloride.

If the dishes are removed direct from the water-bath to the flame for ignition decrepitation is sure to result. To guard against this place

the dish in the air-bath at a temperature of 100° C. and gradually raise to 120° C., and then ignite over a moving flame.

The heating must not be too strong as potassium chloride is volatile. To test its freedom from ammonia salts, the residue of mixed chlorides, after weighing, should be again heated and weighed, to see if further loss occurs.

This operation should be repeated until the weights are constant.

Volumetric or Cobalti-Nitrite Method for Potash[1]

Cobalti-Nitrite Solution:—Dissolve 220 grams of sodium nitrite in 400 cc. of water. Dissolve 113 grams of cobalt acetate in 300 cc. of water and 100 cc. of glacial acetic acid. Mix the two solutions in a flask and gently warm. A dark precipitate and NO_2 are formed. Evacuate the NO_2 fumes by attaching the flask to a Bunsen water-pump and let stand over night. Filter the solution and make up to 1,000 cc. Keep this solution in a dark bottle.

Tenth Normal Permanganate:—Dissolve 3.156 grams of pure potassium permanganate in one liter of water. Standardize with sodium oxalate[2] (U. S. Bureau Standards). One cubic centimeter of tenth normal permanganate = 0.0008573 gram of potash, K_2O. One cubic centimeter tenth normal permanganate = 0.0067 grams sodium oxalate. Hence to standardize use 0.134 gram of sodium oxalate which should require about 20 cc. of the permanganate. If the above exact weight of sodium oxalate is taken, then if B cubic centimeters of the permanganate are required for the titration.

$$\text{One cc. of permanganate} = \frac{20}{B} \times 0.0008573 \text{ grams } K_2O.$$

It is unquestionably best to standardize the permanganate against pure potassium chloride. Weigh exactly 0.0271 grams of pure fused KCl (equivalent to 0.01715 gram of K_2O) into a dish dissolve in a little water, make slightly acid with acetic acid and proceed as directed below by evaporating to pasty consistency and adding cobalti-nitrite solution, etc.

Tenth-Normal Oxalic Acid:—Dissolve 6.3 grams of pure recrystallized oxalic acid in one liter of water and check against the N/10 permanganate.

[1]Method worked out in the Laboratory of the Security Cement and Lime Co., Security, Md., R. B. Haft, Chemist.

[2] See page 454 for procedure.

Determination

For the determination of potash by this method in cement, clinker or raw material employ a two gram sample and add one-half gram of ammonium chloride and 4 grams of calcium carbonate and proceed as described in J. Lawrence Smith's method.

For the determination of potash in treater-dust and stack-encrustations, use a 0.5 gram sample and add one quarter gram of ammonium chloride and 4 grams of calcium carbonate and proceed as in J. Lawrence Smith's method.

After the mass has been ignited place in a small (4″) casserole and add hot water. Set on the hot plate and heat gently. When the mass has slaked to a fine powder filter into a flat bottom porcelain dish, washing the filter three or four times with very hot water. Make the filtrate slightly acid with acetic acid and evaporate to dryness on a water-bath. Heat until no odor of acetic acid remains and dissolve the dry residue in the dish in about 5 cc. of hot water, taking care to wash the sides of the dish thoroughly.

Now add from 10 to 15 cc. of the Cobalti-Nitrite solution. There should be about 10 cc. of reagent for every 0.03 gram of potash present. Evaporate the mixture on a steam bath to pasty consistency. Remove from the bath and when cold add about 30 cc. of *cold* water, breaking up the precipitate with a glass rod. Filter through an asbestos filter[1] and wash precipitate once with *cold* water. The water should be poured from a beaker not squirted from a wash bottle.

Wash filter and contents into a 400 cc. beaker in which has been previously placed an excess of the N/10 permanganate (15 cc. for each 0.01 gram of K_2O) diluted to 150-200 cc. with hot water and stir to break up the filter. Place the beaker and contents on the steam bath and heat for at least 15 minutes, or until a decided black color appears. Acidulate with 10 cc. of 1:1 sulphuric acid and add sufficient of the N/10 oxalic acid from a burette or pipette to clear the solution. When the solution is clear titrate the excess of oxalic acid against the standard permanganate. The total permanganate used, less the oxalic acid used, multiplied by the factor for the permanganate gives the potash.

[1] For this filter see pages 450 and 472.

Or, $(A + C - E)F$ = weight of K_2O in sample.

When,

A = cc. N/10 permanganate required for first titration.

B = cc. N/10 oxalate required to reduce above.

C = cc. N/10 permanganate required to oxidize excess of oxalic acid.

D = Factor for converting N/10 oxalic acid to N/10 permanganate.

F = Potash equivalent to 1 cc. of permanganate.

E = B $\times$ D.

For example:—The permanganate was found to be 1.01 tenth normal. Hence 1 cc. = 0.0008658 grams of K_2O. Ten cc. of oxalic acid required 10.3 cc. of permanganate. Hence 1 cc. oxalic acid = 1.03 cc. of permanganate. In the actual determination a 2 gram sample was used. Twenty cc. of permanganate was originally used and 10 cc. of oxalic acid were required to clear (Equivalent to 10.3 cc. of permanganate). 6.1 cc. of permanganate were then required to back titrate. The potash was therefore found to be $(20 + 6.1 - 10.3) \times 0.0008658 = 0.01368$ gram or $0.01368 \div 2 = 0.68$ per cent.

NOTES

This method is only applicable when potash determinations have to be made daily as where potash is recovered from the kilns, etc. It should be carefully compared with the results obtained by gravimetric methods.

DETERMINATION OF PHOSPHORIC ACID

Weigh 5 grams of cement into a dry beaker and stir with 15 cc. of water until all lumps are broken up. Add from 30 to 50 cc. of hydrochloric acid (sp. gr. 1.20) cover with a watch-glass and heat until the cement is decomposed. Remove the cover, evaporate to hard dryness on the hot plate, and heat for from thirty minutes to one hour longer. Redissolve in 30 cc. of hydrochloric acid (sp. gr. 1.29) and evaporate to pasty consistency. Add 30 cc. of nitric acid (sp. gr. 1.42) and evaporate to 15 cc. Dilute with 30 cc. of water, heat, filter through a small filter and wash. Add ammonia until a slight precipitate forms, and then 3 cc. of concentrated nitric acid. The solution should now be am-

ber-colored. Add 80 cc. of molybdate solution, heat to 80° C., and stir for five minutes. Let the solution stand one hour. Filter and wash well with acid ammonium sulphate solution. Dissolve the precipitate in the least possible quantity of dilute ammonia (1 : 5) and allow the solution to run into the beaker in which the precipitation was made. Wash the paper well with cold water. The filtrate should be clear and colorless. (If cloudy add hydrochloric acid until the liquid is acid, this usually precipitates the phosphomolybdate, then four or five drops of a concentrated solution of citric acid and finally ammonia until strongly alkaline.) To the filtrate add slowly with constant stirring an excess of magnesia mixture. Stir for five minutes, then add one-third the volume of the solution of strong ammonia and allow to stand three or four hours. Filter, wash with a mixture of water 1,000 cc., ammonia 500 cc., and ammonium nitrate 150 grams, dry, ignite, and weigh as $Mg_2P_2O_7$. To convert this weight to phosphorous pentoxide, P_2O_5 multiply by 0.63780.

NOTES

The solutions called for in the scheme are prepared in the following manner:

Molybdate Solution: Mix in a beaker 20 grams of pure molybdic acid with 80 cc. of cold distilled water and add 16 cc. of ammonia (sp. gr. 0.90). When solution is complete, filter and pour slowly into a mixture of 80 cc. of nitric acid and 120 cc. of water.

Ammonium Sulphate Solution: Add 15 cc. of ammonia (sp. gr. 0.90) to 1,000 cc. of water and then 25 cc. of concentrated sulphuric acid (1.84 sp. gr.).

Magnesia Mixture: Dissolve 11 grams of crystallized magnesium chloride in water (or 2.2 grams of calcined magnesia in dilute hydrochloric acid avoiding an excess), filter, add 28 grams of ammonium chloride, 70 cc. of ammonia (sp. gr. 0.96), and enough water to make 200 cc. Filter before using.

DETERMINATION OF MANGANESE

Colorimetric Method

Stir 0.2 gram of cement with 10 cc. of water until all lumps are broken up, add 10 cc. of dilute (1 : 1) nitric acid and heat until solution is complete and all nitrous fumes are driven off. Now add 15 cc. of silver nitrate solution (containing 1.33 grams of

silver nitrate to the liter of water). This will cool the solution considerably. Add at once about 1 gram of ammonium persulphate and warm until the color commences to develop and then for about half a minute longer. Placing the beaker in cold water until the evolution of oxygen ceases and then pour into a graduated Nessler tube. Into another cylinder from 1-3 cc. of a standard solution of manganese (made by dissolving 0.0556 gram of crystallized potassium permanganate in 500 cc. of water. Strength 1 cc. = 0.00005 gram MnO) is measured and the two cylinders stood side by side and viewed *horizontally*—not vertically. Water is then added to the standard to make it match the other tube. The height of the liquid in the two tubes is then read and the percentage of MnO calculated from the formula

$$X = \frac{a \times B \times 0.005}{A \times w}$$

When a = number of cc. of standard solution placed in the cylinder and A the number of cc. to which it is diluted in order to produce the same shade as the cement sample diluted to B cc. W = weight of sample taken or 0.2 gram. It may be necessary where the cement is high in manganese to use a smaller sample than 0.2 gram.

DETERMINATION OF TITANIUM

Colorimetric Method of A. Weller

If titanium is to be determined, follow closely the method of analysis outlined on page 438. Purify the silica with hydrofluoric acid and ignite the iron and alumina precipitate in the same crucible with the residue from this treatment. Dissolve the precipitate, after weighing, in potassium bisulphate by fusion, and then the fused mass in water, acidified with sulphuric acid. Evaporate the fused mass until fumes of sulphuric acid come off. Dilute, filter and saturate the filtrate with hydrogen sulphide gas. Filter from any platinum sulphide and boil off the hydrogen sulphide in a current of carbon dioxide. Determine the iron by titration with potassium permanganate as described on page 459.

Concentrate the solution, after the titration is completed, to 50 cc. and transfer to a 50 cc. Nessler tube. Add 2 cc. of 3 per

cent hydrogen peroxide, absolutely free from fluorine. This produces an intense yellow color which is proportional to the amount of titanium present. Compare this color with that produced by hydrogen peroxide upon various volumes of a standard solution of titanium prepared as follows: Gently ignite potassium titanic fluoride and weigh 0.6000 gram of this into a platinum crucible. Add a little sulphuric acid and water, evaporate to dryness and expel the acid by gentle ignition. Repeat this process, and then dissolve in a little concentrated sulphuric acid and dilute to 200 cc. with 5 per cent sulphuric acid. One cc. of this solution is equivalent to 0.001 gram of TiO_2 or to 0.2 per cent when a half gram sample has been used. In comparing the colors measure into different tubes 0.5 cc., 1.0 cc., 1.5 cc., etc., portions of the standard titanium solution, dilute to the mark, and add 2 cc. of hydrogen peroxide to each. Compare with the color produced by the sample, making up new standards when the color lies between two of the above tubes, etc.

The method is accurate to about 0.01 per cent when a ½-gram sample is taken.

CHAPTER XI

THE ANALYSIS OF CEMENT MIXTURES, SLURRY, ETC.

Since the success of cement making depends primarily upon the proper portion of carbonate of lime to silica and alumina in the cement mixture, it is highly important to be able to rapidly estimate this ratio. If the materials from which the mixture is made are of normal consitution a determination in it of the calcium carbonate alone will suffice to check the correctness of the mixture.

For rapidly checking the percentage of calcium carbonate, two methods are in general use, the alkalimetric method in which the calcium carbonate is decomposed by a measured quantity of standard nitric or hydrochloric acid and the excess of acid determined by titration with standard alkali, and the indirect gas method in which the carbonate of lime is decomposed by acid and the evolved carbon dioxide gas collected in a suitable apparatus and measured; since the CO_2 is proportional to the $CaCO_3$, the percentage of lime can be calculated from the volume of CO_2. For the latter method the Scheibler's calcimeter is used. Neither of these methods gives very accurate results, and when the exact composition of the mixture is desired resort must be had to one of the longer gravimetric methods given further on.

In this country, the acid and alkali method is used almost exclusively to check the composition of the mixture of raw materials, while in England and Germany the method in which the carbon dioxide is measured is employed by many chemists for this purpose.

When the slurry of the wet process is analyzed it should first be evaporated to dryness, then finely pulverized in a mortar and, if intended for complete analysis, again dried for an hour at 110° C. It will then be free from moisture and ready for analysis.

SAMPLING, ETC.

For the control of the composition of the mixture of raw materials it is usual to take samples at certain places during the grind-

ing. In the dry process this is usually done either after the material leaves the ball mills, if these are used to do the grinding, or after the Hercules mills, if they are installed for this work. It is usual to further check the composition of the raw material after it leaves the tube mills. The sample taken from any of the above sources will need further grinding but it is not usual to dry it, unless a complete analysis is to be made. Since either of the rapid schemes given below are affected by the fineness to which the sample is ground, it should be prepared the same way each time, usually by passing all of it through a 100-mesh test sieve. In the writer's practice the sample from the ball mills is taken by an automatic sampler which will be described further on, and brought to the laboratory in a small tin bucket. The sample is spread out on a piece of paper, after a thorough mixing by rolling back and forth on the paper, and divided into 15-20 squares with the point of a spatula. Two or 3 grams are taken from each of these squares and the main sample is then thrown away. The sample of from 50-100 grams is now made to pass a 100-mesh sieve, using a large wedgewood mortar to do the grinding. The finely ground sample is then mixed and 10-20 grams of it placed in a coin envelope or small bottle and taken to the chemical laboratory. The wedgewood mortar answers the purpose much better than an agate one would and, with the soft rock of the Lehigh District, does not contaminate the sample with silica to an amount which can be detected.

The following sampler, Fig. 147, was devised by the writer with the assistance of Mr. Owen Hess, Superintendent of the Dexter Portland Cement Co. It consists of a sheet iron cone, of the dimensions shown, having a rectangular tube inserted at one point in its sides. The cone slips into a piece of 4-inch pipe which in turn revolves in a rigid pillow block. The cone is revolved by the bevel gear arrangement shown, which is run from one of the mill shafts by a sprocket and chain, so as to make two or three revolutions per minute. The sampler is placed below an overhead screw conveyor carrying the ground material from the ball mills to the tube mill bins. A hole is cut in this conveyor trough, so that a stream of this material falls into the cone, striking the

side of the latter about 2 inches from the rim. As the cone revolves the material falls into the cone and passes down through the hollow shaft into a pipe, which carries it back into the main elevator or one of the tube mill bins. When, however, the tube

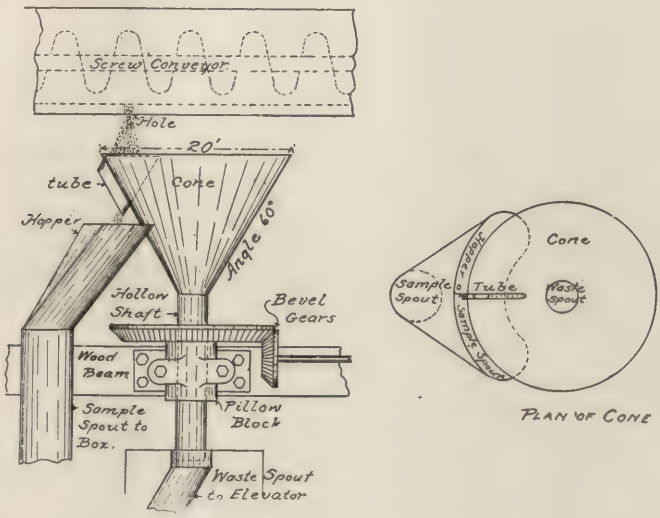


Fig. 147.—Automatic sampler.

comes under the stream, it is deflected out of its course for a moment and passed through this tube down another pipe into a sample bucket placed at a convenient place. The frequency with which the sample is taken will depend on the number of revolutions per minute the cone makes. The amount will depend on the width of the inserted tube and the circumference of the cone. The sampler works well except when the raw material is *very* wet when the pipes clog up.

Where samples have to be taken from a belt conveyor, the appliance shown in Fig. 148 will be found most reliable. This sampler was devised for use in the mills of the Universal Portland Cement Co. and has been in service for some years, giving entire satisfaction. It consists of a spiral, *a*, made of brass pipe both ends of which are left open. This spiral is mounted so as to revolve around a horizontal axis, *d*, above the belt con-

veyor. The height of the axis should be such that the end, *b*, of the spiral just clears the belt. The spiral should be of such length and pitch that one end, *b*, will have its path in a vertical plane passing through the center line of the belt, while the other end, *e*, will extend beyond the conveyor, as shown in the illus-

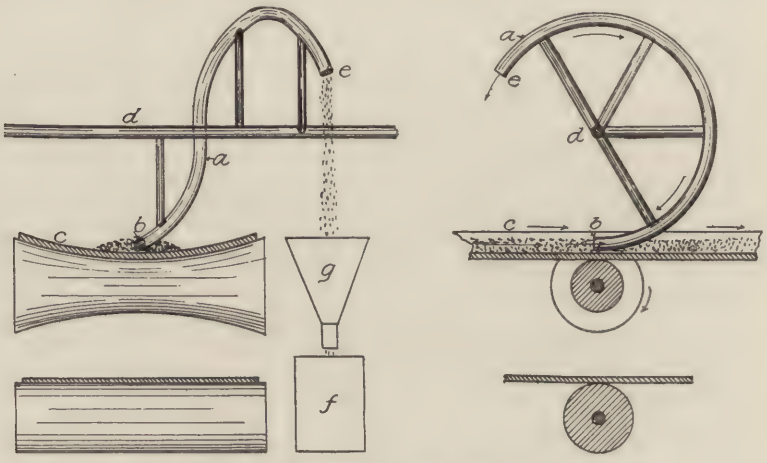


Fig. 148.—Spiral sampler for use with belt conveyors.

tration. The spiral revolves and the belt moves in the directions shown by the arrows. The shaft is usually run by means of a sprocket on the shaft and one on the idler joined by a chain.

When the spiral revolves and the belt moves, the two are going in opposite directions. The end, *b*, of course, each time the spiral revolves, comes down close to the belt and scoops up a little bit of the material being conveyed upon the latter. This material is made to travel through the spiral by the revolutions of the latter and is finally discharged at, *e*, and falls through a chute, *g*, into a sample box, *f*.

In hand sampling from the ball mill, care must be taken not to get a false proportion of fine and coarse material in the sample. The best place to sample is from the conveyor leading from the mills, using a scoop made by tacking a piece of tin, three-quarters of the way around, a piece of board 1½ inches square and 8 or 10 inches long as shown in Fig. 149. Never put the hand inside a

screw conveyor while revolving, as loss of the member may result. A sample of cement-rock limestone mixture, after leaving the

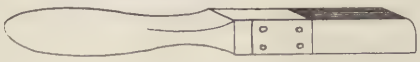


Fig. 149.—Scoop for sampler.

mills, will usually contain from 0.05 to 0.3 per cent moisture, so that for control and check purposes drying of the sample seems unnecessary.

In the wet process, the analytical methods for checking the composition of the slurry are practically the same as in the dry, but on the other hand, the sampling can not be done the same way and the sample itself must be freed from a large amount of water from the mixing pits, and also after the slurry has passed through the tube mills, either from the discharge of the mill itself or else from the slurry pits.

The methods of sampling employed by the chemists at the various mills differ as the following will show:

Mr. W. H. Hitchcock of the Egyptian Portland Cement Co., took samples from the mixing pit, by means of a pint cup, fastened to the end of a wooden pole by means of a wire. It is put in the slurry bottom side up, pushed down to the required depth, about the middle of the pit, and drawn up. As the pole is pulled, the cup rights itself and fills. Each pit holds 170 cubic yards and is sampled in twenty places. The sample is then put in a miniature tube mill and ground for ten minutes. From 25-35 grams of this sample are spread on a thin piece of cardboard and dried at 100° C., after which it is ground in an agate mortar when it is ready for the check determinations.

Mr. N. S. Potter, Jr., of the Peninsular Portland Cement Co., takes his sample from the slurry tanks, which are 16 feet deep, by means of a two-quart tin pail, attached to the end of a pole by a common harness snap. The pail is pushed down into the slurry, bottom up, and full of air. At the desired point the pole is given

a slight jerk when the pail rights, allows the air to escape and fills with the marl or slurry, as the case may be. The sample is then spread out on a piece of paper and dried on the hot-plate.

Mr. Frank I. Post, of the Wolverine Portland Cement Co., uses a special form of sampler, consisting of a cup with two fly valves, one at the top and another at the bottom, attached to a pole. When the sampler is thrust down through the slurry, both valves open and the marl simply runs through the cup, but when the sampler is raised the valves shut, thus enclosing a sample in the

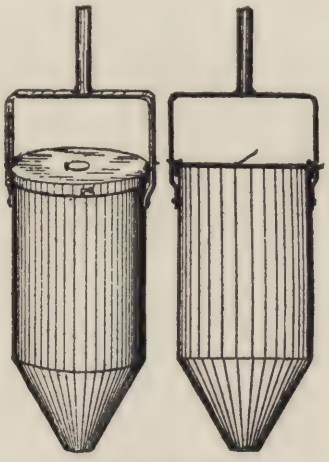


Fig. 150.—Marl sampler.

cup. In removing this sampler from the tank care must be used not to lower it at all. If this is done, the valves of course, open and the sample previously taken is lost, and in its place will be a new sample from the point of lowering.

Fig. 150 shows a marl sampler of the above order described in *The Cement Record.* It is made of tin and the top is held in place by a bayonet catch. Flap valves are fastened to the top and bottom by hinges, the former opens outward and the latter inward. It is used as described above.

Mr. Homer C. Lask, of the Omega Portland Cement Co., also makes use of a bucket with a valve in sampling marl. His apparatus consists of a heavy iron bucket, 3 inches in diameter and

9 or 10 inches long. It has a valve in the bottom, which opens as the bucket sinks through the marl, but closes as soon as it is started in the opposite direction. A sample can thus be taken at any depth desired. The sampler is attached to a rope and sinks into the marl by its own weight. It is withdrawn by means of a small windlass. From three to five samples are taken from a tank, the different samples mixed together, and the whole taken as the tank sample.

The slurry is sampled, automatically, as it leaves the tube mill by an ingenious device. The tube mills at this plant have a central discharge and on the inner surface of the discharge conduit is attached a stout cup, of about 1 cubic inch capacity, with its open end towards the stream of slurry as the mill makes its revolution. The cup fills as it passes through the stream of slurry and discharges as it is carried over the top. A portion of the discharge is allowed to fall into a small trough, down which it flows into a bucket. This bucket holds about four pints and the sampler is so gauged that the former will fill in about an hour.

Samples of slurry and marl may also be taken by agitating the vat or tank thoroughly and then taking two or three small samples from the elevator or pump discharge, and mixing and grinding the sample obtained.

In order to correct the composition of slurry found to be under or overclayed, it is necessary to know not only how much carbonate of lime it contains, but also how much water. To determine the latter the usual rule is to evaporate a weighed portion of the slurry to dryness and determine the loss in weight. This evaporation can be carried on most rapidly and also safest on an electric hot-plate or oven, the temperature of which can be regulated. A "radiator" may also be used consisting of a round sheet iron box, with an open top and bottom flanged on. It is made of any convenient dimensions and usually with its diameter at the top a little larger than at the bottom. Convenient dimensions are 6 inches deep, 5½ inches diameter at the top and 4½ inches diameter at the bottom. The radiator will then set in the ring of a 5-inch tripod. The substance to be evaporated is held on a triangle support, midway between the top and bot-

tom of the box and made of heavy copper or iron wire. Fig. 151 shows the apparatus, which is to be heated by a burner.

Practically the same results can be arrived at by using a round sheet iron cylinder, 6 inches high and 5 inches in diameter with a

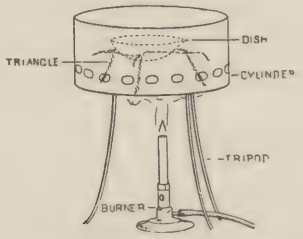


Fig. 151.—Radiator for drying slurry samples.

support 3 inches from the bottom, and setting over the hottest part of the hot-plate. An ordinary porcelain dish may be made use of to hold the sample but a flat dish of tin or aluminum or even a flat sheet of thin sheet iron or aluminum with a corner turned up to serve as a handle will serve the purpose better. Not only because greater surface is exposed but also because metal is a better conductor of heat than porcelain. As a quick test to determine when all the water is driven off, hold a cold watch-glass over the dish and observe if any moisture collects on it.

If 16.88 cc. of slurry are taken for evaporation each 0.01 gram of dried residue will represent the number of pounds of dried slurry in a cubic yard of the wet slurry. This amount may be measured by means of a small pipette made to hold exactly this amount to the mark. In use the pipette must be washed out with a jet of water from a wash-bottle. Or 6.25 cc. may be taken when 0.1 gram will represent pounds per cubic foot, etc. When organic matter is present this also acts as a disturbing element in determining the correctness of the composition of the slurry. If constant, allowance can usually be made for it, but when variable the best plan is either to burn this off or else run the mix by a ratio of lime to insoluble.[1]

Mr. A. Lundteigen recommended weighing the dried sample into a small iron tray, which is suspended in a larger one and

[1] See Chapter IV.

this in its turn is covered and put over a good Bunsen burner for twenty minutes. In this way over three-quarters of the organic matter is driven off without decomposing the carbonate. This also puts the sample in such a condition that it will sink in a solution of hydrochloric acid, and be quickly dissolved. Without this baking process the marl used by one company will float on top of the acid and even shaking and boiling will dissolve it only with difficulty. The baked sample, however, is very hygroscopic and takes up moisture rapidly from the air, so it must be weighed quickly.

RAPID METHODS FOR CHECKING THE PERCENTAGE OF CALCIUM CARBONATE IN CEMENT MIXTURES

By Standard Acid and Alkali

Phenolphthalein

Dissolve 1 gram of phenolphthalein in 100 cc. of alcohol (50 per cent). Keep in a small bottle provided with a perforated

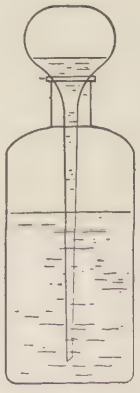


Fig. 152.—Phenolphthalein dropper.

stopper through which passes a small pipette, made from a piece of 5-inch narrow bore glass tubing by drawing out one end to a fine opening, and blowing a bulb in the other, Fig. 152.

One drop of this solution is sufficient for a determination.

Standard Alkali

In order to prepare standard alkali of exactly $^2/_5$ N strength it is necessary to first prepare a standard solution of some acid, preferably of sulphuric, because of the ease with which this can be standardized by precipitation with barium chloride. To prepare this standard acid, measure out with a burette 11.2 cc. of concentrated sulphuric acid (1.84 sp. gr.) and dilute to one liter. Shake well and measure into each of two small beakers 10 cc. of this sulphuric acid and dilute to 100 cc. Add a few drops of hydrochloric acid, heat to boiling, and precipitate the sulphuric acid with barium chloride. Let the precipitate stand over night, then filter through a double filter (or preferably the Shimer filter[1]), wash with hot water, ignite and weigh. Calculate the quantity of this acid equivalent to 10 cc. of $^2/_5$ N sulphuric acid in the following manner. Ten cc. of $^2/_5$ N sulphuric acid should give 0.467 gram of $BaSO_4$. If the average weight of both precipitates is a gram, then letting x represent the number of cubic centimeters containing 0.467 gram of $BaSO_4$.

$$0.467 : a : x : 10 \text{ or } x = \frac{4.67}{a}.$$

Hence $\frac{4.67}{a}$ cc. of our standard acid will be equivalent to 10 cc. of $^2/_5$ N acid. This should be marked on the bottle and the solution put away in a dark cool place for use at any future time.

To prepare the standard alkali, dissolve 175 grams of caustic soda in eight liters of distilled water in a two-gallon bottle (which usually holds nine liters) and mix well by shaking. Now measure into each of two beakers the quantity of our standard sulphuric acid equivalent to 10 cc. of normal acid, and after adding a drop of phenolphthalein solution, run in the sodium hydroxide solution from a burette until the solution turns purple red. The two titrations should check exactly. If not, repeat until they do. Now dilute the caustic soda solution so that it is exactly $^2/_5$ normal.

[1] See page 472.

The number of cubic centimeters of water necessary to add to the caustic soda solution may be found by the formula

$$\left(\frac{10}{b} - \right) \times C$$

when b = cc. soda required to neutralize the equivalent of 10 cc. of $^2/_5$ N acid and C = quantity of caustic soda solution still left in the bottle.

Example of the preparation of the standard $^2/_5$ N alkali.

Weight of 1st $BaSO_4$ precipitate	0.4975
Weight of 2d $BaSO_4$ precipitate	0.4987
Average	0.4981

Therefore $\frac{4.670}{0.4981} = 9.38$ cc. of the acid, are equivalent to 10 cc. of $^2/_5$ N acid.

Now 9.38 cc. of the above acid require 8.7 cc. of caustic soda, as determined by duplicate titrations. As we have used 20 cc. of our caustic soda we will have in the bottle 8,000 — 20 = 7,980 cc. and hence we must add to this $\left(\frac{10}{8.7} - 1\right)$ 7,980 or 1,189 cc. Since our bottle will only hold nine liters it will probably be better to draw off exactly one liter when the amount to be added to the remainder will be $\left(\frac{10}{8.7} - 1\right)$ 6,980 or 1,040 cc. We therefore measure out this quantity of water and add it to the contents of the bottle.

The standard caustic soda solution should now be checked against the acid and, if not of correct strength, water must be added, as indicated, until it is exactly $^2/_5$ N strength.

One cc. of this solution is equivalent to exactly 0.020 gram of $CaCO_3$, or 2 per cent where a 1-gram sample is used. A two-gallon bottle of standard alkali will make at least 2,000 determinations so it pays to make it of correct strength and save calculations.

Standard Acid

Take the specific gravity of a bottle of hydrochloric acid, using a hydrometer for the purpose. Refer to the table of specific gravities of hydrochloric acid given below and calculate from this the quantity of acid necessary to contain 97 grams of HCl.

Measure this quantity of the acid into a liter flask and dilute to the mark, pour into an eight-liter bottle and add seven liters of water, measuring with the flask. Mix the contents of the bottle

well by shaking. Ten cc. of this solution should be equivalent to from 8.1 to 8.5 cc. of the $^2/_5$ N alkali when checked by adding a drop of phenolphthalein solution and running in the alkali to a purple red color. If its value does not lie between these figures add acid or water to make it of this strength.

TABLE XLIII.—SPECIFIC GRAVITIES OF HYDROCHLORIC ACID

Sp. gr. at 15° C.	Degrees Baume	Degrees Twadd'l	Per cent of HCl	Grams of HCl in 1 liter	Correction of the sp. gr. for ± 1° C.
1.005	0.7	1	1.12	11.32	0.0006
1.010	1.4	2	2.12	21.43	0.0006
1.015	2.1	3	3.12	31.67	0.0006
1.020	2.7	4	4.11	41.99	0.0006
1.025	3.4	5	5.11	52.41	0.0006
1.030	4.1	6	6.11	62.93	0.0006
1.035	4.7	7	7.10	73.55	0.0006
1.040	5.4	8	8.10	84.27	0.0006
1.045	6.0	9	9.10	95.09	0.0006
1.050	6.7	10	10.09	106.01	0.0006
1.055	7.4	11	11.09	117.02	0.0006
1.060	8.0	12	12.09	128.14	0.0006
1.065	8.7	13	13.08	139.36	0.0006
1.070	9.4	14	14.08	150.68	0.0006
1.075	10.0	15	15.08	162.10	0.0006
1.080	10.6	16	16.07	173.63	0.0006
1.085	11.2	17	17.07	185.24	0.0006
1.090	11.9	18	18.07	196.96	0.0006
1.095	12.4	19	19.07	208.78	0.0006
1.100	13.0	20	20.06	220.70	0.0006
1.105	13.6	21	21.06	232.68	0.0006
1.110	14.2	22	22.06	244.80	0.0006
1.115	14.9	23	23.05	257.02	0.0006
1.120	15.4	24	24.05	269.34	0.0006
1.125	16.0	25	25.05	281.76	0.0006
1.130	16.5	26	26.04	294.28	0.0006
1.135	17.1	27	27.04	306.90	0.0006
1.140	17.7	28	28.04	319.62	0.0006
1.145	18.3	29	29.03	332.44	0.0006
1.150	18.8	30	30.03	345.36	0.0006
1.155	19.3	31	31.03	358.34	0.0006
1.160	19.8	32	32.02	371.44	0.0006
1.165	20.3	33	33.02	384.64	0.0006
1.170	20.9	34	34.02	397.94	0.0006
1.175	21.4	35	35.01	411.34	0.0006
1.180	22.0	36	36.01	424.84	0.0006
1.185	22.5	37	37.01	438.44	0.0006
1.190	23.0	38	38.01	452.14	0.0006
1.195	23.5	39	39.00	466.00	0.0006
1.200	24.0	40	40.00	479.84	0.0006

Example of the preparation of the standard acid.

On testing a bottle of hydrochloric acid its specific gravity is found to be 1.195° C. at 23° C. Correcting this to 15° C. we have $1.95 + (23 - 15) \times 0.00006 = 1.1998$, or practically 1.20 sp. gr. at 15° C. Hydrochloric acid of 1.20 sp. gr. contains 479.84 grams of HCl per liter or 0.480 gram per cubic centimeter. Therefore $\frac{97}{0.480}$ or 202 cc. will contain 97 grams of HCl, hence we measure out this quantity of acid and dilute to eight liters.

Standard Sample

A standard sample of the raw material is necessary to standardize the acid and alkali for actual use. This sample should be ground in the same manner as the daily run of samples to be checked by the acid and alkali. It should all pass a 100-mesh sieve and be freed from hygroscopic moisture, by drying for some hours, at 110° C. Three of four pounds of this sample should be prepared and kept in air-tight jars or bottles. A small sample (one or two ounces) of this should be placed in a two-ounce bottle and stoppered with a rubber cork when not in use. This small sample can then be redried for an hour at 100°-110° C. and used for standardizing, avoiding the frequent opening and mixing of the contents of the large jars or bottles.

After drying, the standard sample should be carefully analyzed. It should contain approximately the quantity of carbonate of lime which it is desired to have in the mix, and the amount of magnesia should also be normal. When the magnesia varies at different times fresh standard samples should be prepared to contain these varying percentages of magnesia; otherwise the lime will be reported too high.

Standardizing the Acid

Weigh 1 gram of the standard sample into a 600 cc. Erlenmeyer flask and run in from a pipette 50 cc. of standard acid. Close the flask with a rubber stopper, having inserted through it a long glass tube 30 inches long and about ⅜-inch internal diameter. Heat the flask on a wire gauze over a burner as shown in Fig. 153 until steam *just begins* to escape from the upper end of the tube. The heating should be so regulated, that the operation requires very nearly two minutes, from the time the heat is

applied, until steam issues from the tube. Remove the flask from the heat, as soon as the steam escapes from the tube, and rinse the tube into the flask, in the following manner. Rest the flask, still stoppered, on the table and grasp the tube between the thumb and forefinger of the left hand. Direct a stream of cold water, from a wash-bottle in the right hand, down the tube, hold

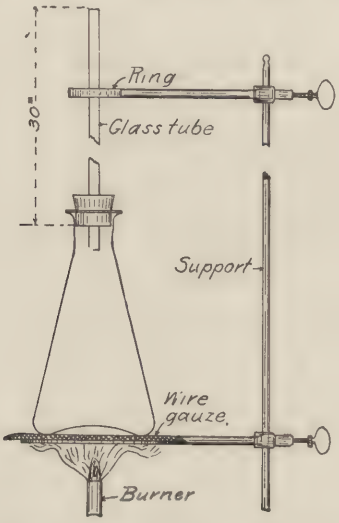


Fig. 153.—Apparatus for determining calcium carbonate with acid and alkali.

ing the latter inclined at an angle 45°, and rolling the flask from side to side on the table, in sweeps of 2 or 3 feet, by twirling the tube between the finger and thumb. Unstopper the flask and rinse off the sides and bottom of the stopper, into the flask, and wash down the sides of the latter. Add a drop or two of phenolphthalein and run in the standard alkali, from a burette, until the color changes to purple red. This color is often obscured until the organic matter settles, so it is necessary to hold the flask to the light and observe the change by glancing across the surface. A little practice will easily enable the operator to carry on the titration with accuracy and precision.

If the standard sample contains L per cent carbonate of lime and d cc. of alkali are required to produce the purple red color,

then to find the carbonate of lime in other samples it is only necessary to subtract the number of cubic centimeters of alkali required in their case from *d*, multiply the difference by 2 and add to L, for the percentage of carbonate of lime in them; or if the number of cc. is greater than *d*, subtract *d* from this number, multiply by 2 and subtract from *L* for the carbonate of lime.

In order to avoid all calculations prepare a table giving the various percentages of carbonate of lime corresponding to different quantities of alkali.

Example of Such a Table: Suppose the standard sample contains 75.0 per cent carbonate of lime and 4.6 cc. of standard alkali are required to produce a purple red color. Then since each cc. of alkali is equivalent to 0.02 gram or 2 per cent of carbonate of lime 4.5 cc. alkali would represent 75.2 per cent carbonate of lime and 4.4 cc. alkali would be equivalent to 75.4 per cent carbonate of lime. Similarly 4.7 cc. alkali are equal to 74.8 per cent carbonate of lime. So we see the lime progresses by 0.2 per cent for each decrease of 0.1 cc. alkali and we can quickly write the following table:

Cc. alkali	Per cent $CaCO_3$	Cc. alkali	Per cent $CaCO_3$	Cc. alkali	Per cent $CaCO_3$
3.8	76.6	4.5	75.0	5.2	73.8
3.85	76.5	4.55	75.1	5.25	73.7
3.9	76.4	4.6	75.0	5.3	73.6
3.95	76.3	4.65	74.9	5.35	73.5
4.0	76.2	4.7	74.8	5.4	73.4
4.05	76.1	4.75	74.7	5.45	73.3
4.1	75.0	4.8	74.6	5.5	73.2
4.15	75.9	4.85	74.5	5.55	73.1
4.2	75.8	4.9	74.4	5.6	73.0
4.25	75.7	4.95	74.3	5.65	72.9
4.3	75.6	5.0	74.2	5.7	72.8
4.35	75.5	5.0	74.1	5.75	72.7
4.4	75.4	5.1	74.0	5.8	72.6
4.45	75.3	5.15	72.9	5.85	72.5

Determination

Weigh 1 gram of the sample, which has been ground to pass a 100-mesh sieve, into the flask, add 50 cc. of the standard acid and proceed as directed under standardizing the acid. The percentage of carbonate of lime may be found from the number of cc. of alkali used either from the preceding table or by the formula

$$\% \ CaCO_3 = L + (d - S) \times 2.$$

Where L and *d* have the same values as in the paragraph on

"Standardizing the Acid" and S represents the number of cubic centimeters required for the sample whose composition is desired. If 4.25 cc. of alkali are required then the sample contains $75 + (4.6 - 4.25) \times 2 = 75.7$ per cent carbonate of lime.

NOTES

The process depends upon the decomposition of calcium carbonate by a measured quantity of standard alkali in excess of that required by theory and then determining the excess acid by titration with standard alkali.

$$CaSO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$
$$HCl + NaOH = NaCl + H_2O.$$

Hence, 1 cc. of $^2/_5$ normal acid will decompose 0.02 gram of $CaCO_3$ and 1 cc. of $^2/_5$ normal acid will neutralize as much acid as 0.02 gram of $CaCO_3$.

Phenolphthalein is a very delicate indicator. It is, however, very susceptible to carbon dioxide and the solution must be freed from the latter by boiling whenever this indicator is used. It is also useless in the presence of free ammonia or its compounds. The addition of a few drops of the indicator to an acid or neutral solution shows no color, but the faintest excess of caustic alkali gives a sudden change to purple red. Methyl orange may be used in place of phenolphthalein. While not so delicate it possesses certain advantages over the latter. It can be used in the cold with carbonates, and its delicacy is not impaired by the presence of ammonia or its salts. A convenient strength for the methyl orange indicator is 0.1 gram of the salt to 100 cc. of water. One drop of this solution is sufficient for 100 cc. of any colorless solution. Alkaline liquids are faintly yellow with methyl orange and acid ones are pink. Of the two indicators, however, phenolphthalein is much to be preferred for this work, as the carbon dioxide has all been boiled off the acid and provided the alkali is properly kept, the amount in this is constant and hence exercises the same influence all the time.

Standard $^2/_5$ N caustic soda may be prepared, however, free from carbon dioxide, by the following method: Take about twice the quantity of caustic soda required for the standard solution, dissolve in water and add 25 grams of freshly slaked lime made into a milky paste with water. Boil for ten or fifteen minutes and, when cool enough to avoid cracking the latter, pour into a five-pint bottle. Add water enough to nearly fill the bottle, stopper, shake and let stand over night to settle. In the morning, siphon off the clear liquid and make up to five or six liters. Run against the standard sulphuric acid solution and dilute with freshly boiled distilled water as directed above for the preparation of $^2/_5$ N alkali.

As a preliminary standard for the preparation of the $^2/_5$ N alkali, hydrochloric acid may be used instead of sulphuric acid. It is more troublesome to standardize, however. Prepare the $^2/_5$ normal hydrochloric acid as directed in the scheme and standardize gravimetrically as follows:

To any convenient quality of the acid to be standardized, add solution of silver nitrate in slight excess, and 2 cc. pure nitric acid (sp. gr. 1.2). Heat to boiling-point, and keep at this temperature for some minutes without allowing violent ebullition, and with constant stirring, until the precipitate assumes the granular form. Allow to cool somewhat and then filter through asbestos. Wash the precipitate by decantation, with 200 cc. of very hot water, to which has been added 8 cc. of nitric acid and 2 cc. of dilute solution of silver nitrate containing 1 gram of the salt in 100 cc. of water. The washing by decantation is performed by adding the hot mixture in small quantities at a time, beating up the precipitate well with a thin glass rod after each addition. The pump is kept in action all the time; but to keep out dust during the washing, the cover is only removed from the crucible when the fluid is to be added.

Put the vessels containing the precipitate aside, return the washings once through the asbestos so as to obtain them quite clear, remove from the receiver, and set aside to recover the silver. Rinse the receiver and complete the washing of the precipitate with about 200 cc. of cold water. Half of this is used to wash by decantation and the remainder to transfer the precipitate to the crucible with the aid of a trimmed feather. Finish washing in the crucible, the lumps of silver chloride being broken down with a glass rod. Remove the second filtrate from the receiver and pass about 20 cc. of alcohol (98 per cent) through the precipitate. Dry at from 140° to 150°. Exposure for half an hour is found more than sufficient at this temperature, to dry the precipitate thoroughly. The weight of silver chloride multiplied by 0.25424 gives the hydrochloric acid in the volume taken.

Instead of $^2/_5$ normal caustic soda the corresponding $^2/_5$ normal caustic potash may be used. To prepare, substitute 220 grams of KOH for 175 grams of NaOH, and proceed as directed in the scheme.

The standard hydrochloric acid used in the determination itself is not exactly $^2/_5$ normal; in fact, is much weaker than this. It is made so in order to avoid waste of the alkali. If made $^2/_5$ normal strength, it would require about 12.5 cc. of alkali to titrate back. A smaller pipette might be used or the acid measured with a burette. The automatic pipettes are usually made in sizes, 25 cc., 50 cc., etc., and are so convenient for measuring the acid that, as there is nothing to be gained by making the acid $^2/_5$ normal strength, it will be found more convenient to make it of the strength indicated in the scheme, and use a 50 cc. automatic pipette.

In some laboratories, the acid and alkali are both made of $^1/_5$ N strength and a half gram sample is used for the determination. There appears to be nothing gained by this and something may be lost as the stronger acid is a better solvent for the sample.

The bottle of strong hydrochloric acid, used to make the standard acid, should be marked with the number of cubic centimeters required to make eight liters of standard acid and put away for use in making up the next lot of acid.

In preparing a second lot of acid it will save calculation and the preparation of a new table, if the acid is made up to the same strength as before. To do this make a little weaker than the figures call for and

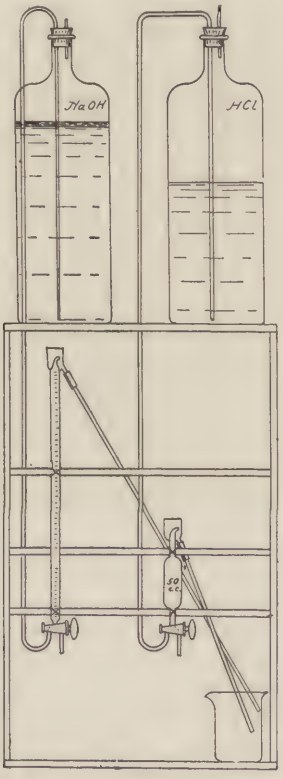


Fig. 154.—Stand for acid and alkali bottles and pipettes.

ascertain its strength by a trial determination on the standard sample, then, if too much carbonate of lime is found, add acid cautiously until

the value of a determination made with the standard sample shows the proper percentage of lime.

Standard nitric acid may be used in place of the standard hydrochloric acid. It keeps better and is not quite so volatile, but, on the other hand, is not so good a solvent. On the cement-rock mixtures of the Lehigh District hydrochloric acid works best, but nitric acid is used in the laboratories of several wet process mills in the west. The nitric acid is prepared exactly as is the hydrochloric acid, using such a quantity of strong acid, however, as will contain 167 grams of HNO_3.

Fig. 154 shows a convenient way of arranging the bottles, burette and pipette for the acid and alkali. Its construction is so evident from the drawing that a description seems unnecessary. Both the burette and pipette are of the Eimer and Amend automatic zero pattern. Fig. 155 shows the pipette in detail.

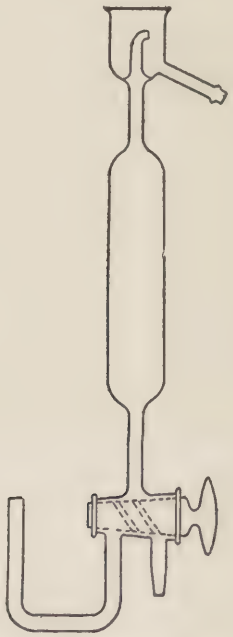


Fig. 155.—Automatic pipette.

The object of the long glass tube is that of a condenser to catch any volatilized acid. This may be replaced by a Leibig's return condenser cooled by water or by a tube full of glass beads, which are wet before the determination with cold distilled water.

A water cooled condenser which is used in the laboratory of the Cowell Portland Cement Co., Cowell, Cal., is shown in Fig. 156. It is made of ordinary iron pipe. The condensers, *a*, *a*, *a*, *a*, contain each a glass tube, *b*, *b*, *b*, *b*, held in place by rubber stoppers. Over the ends of these tubes are slipped rubber stoppers which fit the flasks, *c*, *c*, *c*, *c*.

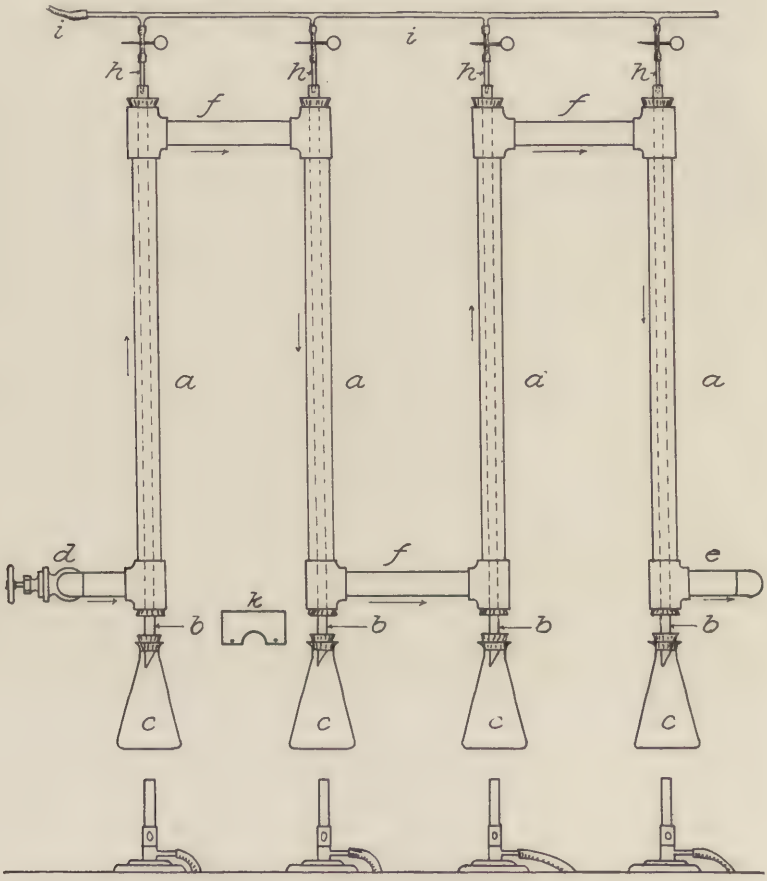


Fig. 156.—Condenser for acid and alkali method.

Water enters at *d*, and flows in the direction of the arrows, being led from one condenser to the next through the side pipes, *f*, *f*, *f*, and finally out at *c*. The flow of water is controlled by the valve, *d*. The glass tube, *i*, is attached to a reservoir of distilled water and the tubes are washed into the flasks by means of the small jets, *h*, *h*, *h*, *h*. This

apparatus will be found very convenient where many determinations are made. If the flasks show a tendency to slip off a small tin collar cut to fit half way around the neck of the flask as shown in *k*, and attached to the tube *a* by a rubber band will serve to keep them on.

Mr. F. H. Ronk, Chemist, Union Portland Cement Co., in a communication to the author states that he dispenses with the long glass tube and other forms of condenser entirely and obtains just as good results by merely boiling the sample for a few minutes in an open Erlenmeyer flask on the hot-plate. The author has also tried this method and found it satisfactory.

A perpetual table for use with any strength acid and alkali may be made as follows: The number of cubic centimeters and twentieths cubic centimeter of alkali from 3 to 8 are written on a piece of stiff paper and pasted fast to a soft pine board. The percentages and tenths of carbonate of lime from 70 to 78 are next written on a piece of cardboard and this is merely fastened to the board with thumb tacks so that the number of cubic centimeters of acid required by the standard sample coincide with the percentage of lime it contains. For instance, in the example given 75 per cent lime are made to coincide with 4.6 cc. of alkali. The board is then to be hung up on the wall behind the alkali burette, etc.

By Measuring the Volume of CO_2 Evolved

At one time, checks upon the composition were made to some extent in this country by means of calcimeters. These all determine the calcium carbonate indirectly by measuring the volume of carbon dioxide given off. These calcimeters are still used extensively in Europe but in this country have been entirely superseded by the simpler and fully as reliable acid and alkali method. The older form of this apparatus was that of Scheibler but with this apparatus tables were necessary in order to correct the volume of gas for various temperatures and pressures. After Lunge invented the compensating tube various improved calcimeters were devised making use of this and doing away with the calculations and tables required by the Scheibler apparatus. It seems probable, however, that none of these calcimeters will find extensive use in this country and most German chemists who have come to American mills have discarded them for the simpler acid and alkali method. Those who are interested in this method of determining lime are referred to the former editions of this book for a description of Scheibler's apparatus and

to Butler's "Portland Cement" and Gatehouse's "Handbook for Cement Work's Chemists" for descriptions of other improved forms used in English and German mills. Marshall's calcimeter is described in Sutton's Volumetric Analysis.

By Permanganate

Weigh 0.5 gram of the sample into a platinum crucible and mix intimately, by stirring with a glass rod, with ¼ gram of finely powdered dry sodium carbonate. Brush off the rod into the crucible with a camel's-hair brush. Cover the crucible and place over a low flame. Gradually raise the temperature until the crucible is red-hot. Then after a minute or two remove to the blast-lamp and ignite for five minutes. Cool the crucible by plunging its bottom in cold water and place in a 400 cc. beaker. Cover with a watch-glass and add 40 cc. of (1 : 4) hydrochloric acid (or 20 cc. of water and 20 cc. of hydrochloric acid, (1 : 1). Heat on a hot-plate until solution is complete. Lift out the crucible with a glass rod, bent in a crook at one end, and rinse it off into the beaker. Heat the contents of the beaker to boiling, add ammonia until alkaline, and then 10 cc. of a 10 per cent solution of oxalic acid, and proceed as directed on page 456.

This method will be found very useful in checking the acid and alkali determinations.

DETERMINATION OF SILICATES

In order to better control the mixture of raw materials it is often of advantage to determine the insoluble matter or silicates. This practice differs considerably at different works, but the following will illustrate the general run of methods.

By Solution and Precipitation

Weigh 0.5 gram of the sample into a porcelain dish or casserole, add 10 cc. of dilute (1 : 1) hydrochloric acid and a few drops of nitric acid, and evaporate to dryness, as rapidly as possible, without spattering. Bake at about 120° C. until all odor of acid has disappeared from the contents of the dish. Cool the latter, add 10 cc. of dilute (1 : 1) hydrochloric acid and cover with a watch-glass. Heat for a few minutes and add 50 cc. of hot water. Boil

a few minutes and add ammonia in faint excess. Boil a little longer, allow to settle and filter. Wash with hot water a few times, ignite and weigh. The residue is called "the silicates" and should, provided the mix is of proper composition, bear a certain ratio to the percentage of carbonate of lime. This ratio varies at different mills, but the figure is usually around 1 : 3.6.

By Solution

Weight 0.5 gram of the mixture into a beaker and boil with 10 per cent hydrochloric acid for five minutes. Filter off the "insoluble matter," wash, ignite and weigh. This method is in use in the laboratories of the Sandusky Portland Cement Co., and the mix is so proportioned as to give a certain ratio between this "insoluble matter" and the lime. This ratio varies at the two mills of the company. At the Sandusky mill the ratio is 3.9 and at the Syracuse mill it is 4.2, the higher ratio being due to the more silicious clay at the latter point.

COMPLETE ANALYSIS OF CEMENT MIXTURE OR SLURRY

Method of the Committee on Uniformity in Analysis of Materials for the Portland Cement Industry of the New York Section of the Society of Chemical Industry

One-half gram of the finely powdered substance is weighed out and strongly ignited for fifteen minutes, or longer if the blast is not powerful enough to effect complete conversion to cement in this time. It is then transferred to an evaporating dish, preferably of platinum for the sake of celerity in evaporation, and the analysis completed as directed on page 438 by moistening with water and digesting with hydrochloric acid, etc.

The above method is tedious and so cumbersome and long as to preclude its use in cement mill laboratories, where samples of the mix are analyzed daily, except for the preparation of standard samples. Even these should be analyzed also by the method in daily use in the laboratory in order to get all the work on the same relative basis and the longer and more accurate results should only be used to check the shorter mill scheme, and to make

sure that the results of the latter are not too wide of the truth. The results which should actually be used as the values for the carbonate of lime, etc., in the samples should be those obtained by the regular mill scheme. If this is not done, acid and alkali will give one set of results and a complete analyses another, etc.

The scheme given below is modeled after those generally in use in cement mill laboratories and combines a fair degree of accuracy with rapidity and convenience of execution.

Method of the Committee on the Analysis of Portland Cement and Cement Materials of the Lehigh Valley Section of the American Chemical Society

Weigh 0.5 gram of the finely ground sample into a small platinum crucible and mix intimately, by stirring with a glass rod, with 0.5 gram of pure dry finely powdered sodium carbonate containing 2 per cent potassium nitrate. Brush off the rod into the crucible with a camel's-hair brush. Cover the crucible and place over a low flame. Gradually raise the latter, until the crucible is red-hot, and continue heating, in the full flame of the Bunsen burner, for five minutes longer; then place over a blast-lamp and heat for five minutes more. Cool and place the crucible on its side in a porcelain casserole or dish, or preferably a platinum dish, and dissolve the mass in 10 cc. of water and 10 cc. of hydrochloric acid. Heat until solution is complete, keeping the dish covered to avoid loss by effervescence. When everything, except a little gelatinous silica, which usually separates out, is in solution, remove the crucible and clean off into the dish with a rubber-tipped rod. Evaporate to dryness at a moderate heat, continuing to heat the mass—not above 200° C.—until all odor of acid is gone. Do not hurry this baking or skimp the time. The whole success of the analysis depends on thoroughness at this point. Cool; add 20 cc. hydrochloric acid (1 : 1); cover, and boil gently for ten minutes; add 30 cc. water raise to boiling, and filter off the silica; wash with hot water four or five times; put in crucible, ignite (using blast for ten minutes), and weight as SiO_2.

Iron and Alumina

Make filtrate alkaline with ammonia, taking care to add only slight excess and boil until odor of ammonia is faint. Filter off the hydroxides of iron and aluminum, washing once on the filter. Dissolve the precipitate with hot dilute nitric acid, precipitate with ammonia; boil five minutes; filter and wash the iron and alumina with hot water once; place in crucible, ignite carefully, using blast for five minutes, and weigh combined iron and aluminum oxides.

Iron

If it is desired to separate the two oxides add 4 grams acid potassium sulphate to the crucible and fuse at a very low heat until oxides are wholly dissolved—twenty minutes at least; cool; place crucible and cover in small beaker with 50 cc. water; add 15 cc. dilute sulphuric acid (1 : 4); cover and digest at nearly boiling until melt is dissolved; remove crucible and cover rinsing them carefully. Cool the solution and add 10 grams powdered C. P. zinc, No. 20. Let stand one hour, decant the liquid into a larger beaker, washing the zinc twice by decantation, and titrate at once with permanganate. Calculate the Fe_2O_3 and determine the Al_2O_3 by difference. Test Zn, etc., by a blank and deduct.

Iron may also be determined by using a separate sample, igniting with half its weight sodium carbonate, dissolving the mass in hydrochloric acid and titrating with stannous chloride as directed on page 463 or the iron may be precipitated with ammonia redissolved in sulphuric acid, and the iron determined by reduction with zinc and titration with permanganate. (See page 457).

Lime

Make the filtrate from the hydroxides alkaline with ammonia; boil; add 20 cc. boiling saturated solution ammonium oxalate; continue boiling for five minutes; let settle and filter. Wash the calcium oxalate thoroughly with hot water, using not more than 125 cc., and transfer it to the beaker in which it was precipitated, spreading the paper against the side and washing down the precipitate first with hot water and then with dilute sulphuric acid

(1:4); remove paper; add 50 cc. water, 10 cc. concentrated sulphuric acid, heat to incipient boiling and titrate with permanganate, calculating the CaO.

Magnesia

If the filtrate from the calcium oxalate exceeds 250 cc.; acidify, evaporate to that volume; cool, and when cold add 15 cc. strong ammonia and with stirring 15 cc. stock solution of sodium hydrophosphate. Allow to stand in the cold six hours or preferably over night; filter; wash the magnesium phosphate with dilute ammonia (1:4) plus 100 grams ammonium nitrate per liter; put in crucible, ignite at low heat and weigh the magnesium pyrophosphate.

Other Constituents

For the determination of sulphur, carbon dioxide, hygroscopic and combined water, and alkalies, refer to the methods given under cement. The fusion method is to be used for determining sulphur which is usually present as sulphide (iron pyrites) or in combination with organic matter in mixtures of marl and clay. Calcium sulphate may be determined by simple solution in hydrochloric acid as in cement.

CHAPTER XVIII

THE ANALYSIS OF THE RAW MATERIALS

METHODS FOR LIMESTONE, CEMENT-ROCK AND MARL[1]

By Ignition of the Sample with Sodium Carbonate

Silica

Weigh 0.5 gram of finely ground dried sample into a platinum crucible and mix intimately with 0.5 gram of pure dry sodium carbonate containing 2 per cent potassium nitrate by stirring with a glass rod. Place the crucible over a low flame and gradually raise this latter until the crucible is red-hot. Continue heating for five minutes, then substitute a blast-lamp for the Bunsen burner and heat for five minutes longer. Place the crucible in a dish or casserole, add 40 cc. of water and 10 cc. of hydrochloric acid, and digest until all the mass is dissolved out of the crucible. Clean off the crucible inside and outside, add a few drops of nitric acid to the solution and evaporate it to dryness. Heat the residue in an air bath or electric oven at 110° C. for one hour, cool, add 15 cc. of dilute hydrochloric acid, cover with a watch-glass and digest for a few minutes on a hot-plate. Dilute with 50 cc. of hot water, heat nearly to boiling, and filter. Wash the residue well with hot water. Dry, ignite, and weigh as silica, SiO_2.

If the limestone is high in silica a trace will be found in the filtrate from the silica as precipitated above. If great accuracy is desired, after evaporation to dryness, dissolve the mass in the dish in hydrochloric acid and water as usual without heating it to 110° C. for one hour and filter and wash. Evaporate the filtrate to dryness, and again dissolve in water and hydrochloric acid, filter, and wash. Ignite the two precipitates together and weigh as SiO_2.

Ferric Oxide and Alumina

Heat the filtrate to boiling, add ammonia in slight but distinct excess, boil for five minutes and filter. Wash the precipitate

[1] The author employs this method for the analysis of composition and slurry.

twice with hot water. Remove the filtrate from under the funnel and in its place stand the beaker in which the precipitation was made. Dissolve the precipitate in dilute nitric acid and wash the filter-paper free from iron with cold water. Heat the solution to boiling and precipitate the iron and alumina with ammonia as before. Filter, allowing the filtrate to run into that from the first precipitation, wash once with hot water, dry and ignite. Weigh and report as ferric oxide and alumina.

If the percentage of ferric oxide and alumina are desired separately, proceed as directed in A, B, C, or D.

A. Ignite 1 gram of the sample with ½ gram of sodium carbonate as directed under silica. Dissolve the sintered mass in dilute hydrochloric acid. Heat to boiling, reduce with stannous chloride and titrate with standard bichromate as directed on page 463.

B. Fuse the precipitate of ferric oxide and alumina, after weighing, with a little sodium carbonate, dissolve in a little water to which a few cubic centimeters of hydrochloric acid have been added, and drop into the solution a few small crystals of citric acid. Add ammonia until the solution smells slightly of the reagent, and then an excess of ammonium sulphide. Allow the black precipitate to settle, filter, wash a few times, dissolve in hydrochloric acid, add a little bromine water, boil awhile and add ammonia in slight but distinct excess. Filter, wash well with hot water, ignite and weigh as Fe_2O_3. Deduct this weight from that of the total ferric oxide and alumina, for the weight of alumina, Al_2O_3.

C. Fuse the precipitate of ferric oxide and alumina, after weighing, with caustic potash in a silver crucible or dish. Treat the fusion with water, boil, filter, and wash. Dry, ignite, and weigh the residue as ferric oxide, Fe_2O_3. Deduct this weight from that of the ferric oxide and alumina, for the weight of alumina, Al_2O_3.

D. Dissolve the residue, after fusion with sodium carbonate, in a little dilute hydrochloric acid and determine the ferric oxide volumetrically by the method given on page 463.

Lime

Heat the filtrate from the iron and alumina, which should measure between 300 and 500 cc., to boiling and add 25 cc. of a saturated solution of ammonium oxalate. Stir and boil for a few minutes and allow the precipitate one hour in which to settle. Filter and wash well with hot water. After washing, treat the precipitate as directed below in *A* or *B*.

A. Punch a hole in the filter-paper and wash the precipitate into the beaker in which the precipitation was formed. Wash the paper with dilute sulphuric acid from a wash-bottle and then with hot water. Dilute the solution to 300 or 400 cc., heat to 60° or 70° C., and after adding 10 cc. of dilute sulphuric acid titrate with permanganate. Calculate the per cent of lime, CaO, or calcium carbonate, $CaCO_3$, in the limestone, as directed under "Volumetric Determination of Calcium," page 455.

B. Dry the precipitate by heating over a low flame, in weighed platinum crucible, ignite until all carbonaceous matter is destroyed and ignite for fifteen minutes over a blast-lamp. Cool and weigh. Again ignite for five minutes over a blast-lamp and weigh. If this weight agrees to within 0.0002 gram of the former one it may be taken as the weight of the calcium oxide, CaO. If it does not agree, ignite again and repeat, if necessary, until the weight is constant.

Magnesia

To the filtrate from the calcium oxalate add sufficient hydrochloric acid to make it slightly acid, and 30 cc. of sodium phosphate solution. Concentrate to about 200 cc. by evaporation. Set the solution in a vessel of cold water and when cooled to the temperature of the latter add ammonia, drop by drop, from a burette, with constant stirring until slightly ammoniacal and the precipitate begins to form. Stop adding ammonia and stir for five minutes, add one-tenth the volume of the liquid of strong ammonia and continue the stirring for three minutes more. Allow the solution to stand in a cool place over night, filter, wash well with a mixture of 1,000 cc. water, 500 cc. ammonia (sp. gr. 0.96), and 150 grams ammonium nitrate. Dry, ignite, and weigh as mag-

nesium pyrophosphate, $Mg_2P_2O_7$. Multiply this by 0.36219 for its equivalent of magnesia, MgO, or by 0.75744 for magnesium carbonate, $MgCO_3$.

By Solution in Hydrochloric Acid

Insoluble Silicious Matter

Weigh 0.5 gram of the finely ground dried sample into a porcelain dish or casserole, cover with a watch-glass and add 30 cc. of water and 10 cc. of concentrated hydrochloric acid. Warm until all effervescence has ceased, uncover, add a few drops of nitric acid, and evaporate to dryness. Bake on the hot-plate or sand-bath until all odor of hydrochloric acid has disappeared, or safer still, heat in an air-bath at 110° C. for one hour after the residue has become perfectly dry. Cool the dish and add 5 cc. of dilute hydrochloric acid, set on the hot-plate, covered with a watch-glass for five minutes, then add 50 cc. of hot water and filter, after digesting until all except silicious matter dissolves. Wash thoroughly, ignite and weigh as "insoluble silicious matter."

Silica

Should it be desirous to know the silica in the "insoluble silicious matter" fuse it with ten times its weight of pure dry sodium carbonate, first over a Bunsen burner turned low, and then, after slowly raising the flame of this latter to its full height, over a blast-lamp until the contents of the crucible are in a state of quiet fusion. Remove the crucible from the lamp and run the fused mass well up on its sides by tilting and revolving the crucible while held with the crucible tongs. While still hot dip the crucible three-quarters of the way up in a pan of cold water which will frequently cause the mass to loosen from the crucible. Wash off any material spattered on the crucible cover into a casserole or dish with hot water, and add the mass in the crucible if it has become detached. If not, fill the crucible with hot water and set on the hot-plate until the fused mass softens and can be removed to the casserole. Dissolve any particles of the mass in hydrochloric acid, that adhere too firmly to the crucible to be removed by gentle rubbing with a rubber-tipped rod. When the hot water has thoroughly disintegrated the fused mass, cover the casserole or dish with a watch-glass and strongly acidify the contents with hydrochloric acid. Heat until all effervescence ceases and everything dissolves except the silica. Wash off the watch-glass into the dish and evaporate the solution to dryness. Heat for one hour at 110° C. in the air-bath, or on the hot-plate at not too high a temperature until all odor of hydrochloric acid has disappeared from the dry mass. Cool, add 10 cc. of hydrochloric acid and 50

cc. of water, warm until all soluble salts are in solution, filter, wash well with hot water, dry, ignite, and weigh as silica, SiO_2.

$$Fe_2O_3, Al_2O_3, CaO, MgO.$$

Mix the two filtrates from the silica separations and proceed to determine iron and alumina, lime and magnesia, as directed in the method "By Ignition with Sodium Carbonate."

When the amount of sodium carbonate added to the "insoluble silicious matter" is greater than 0.5 gram, it is best in very accurate work, instead of mixing the two filtrates from the silica, to determine the iron, alumina, lime, and magnesia in each solution separately, since the large lime precipitate is almost sure to be contaminated with sodium salts if the two filtrates are mixed.

Determination of Organic Matter, Insoluble Silicious Matter, Ferric Oxide and Alumina, Lime and Magnesia.

Weigh 1 gram of the finely ground dried limestone into a porcelain dish or casserole; cover with a watch-glass and add 30 cc. of water and 10 cc. of concentrated hydrochloric acid. Warm until all effervescence ceases, uncover and evaporate to dryness on a water-bath. Heat the dish for one hour, after the residue becomes thoroughly dry, at 110° C. in an air-bath. Cool the dish and add 5 cc. of hydrochloric acid and 50 cc. of hot water. Heat until all soluble salts dissolve, filter upon a Gooch crucible or a small counterpoised filter-paper. Wash well with hot water, dry at 100° C. in an air-bath and weigh as "organic matter" plus "insoluble silicious matter."

Now ignite until all carbonaceous matter is destroyed, and cool and weigh as "insoluble silicious matter." This weight subtracted from the preceding one gives the "organic matter." If the silica in the "insoluble silicious matter" is desired, fuse the latter with ten times its weight of sodium carbonate and proceed as described in the preceding scheme for the analysis of limestone "By Solution in Hydrochloric Acid."

Heat the filtrate from the "organic matter" and the "insoluble silicious matter" to boiling, add ammonia in slight but distinct excess, and proceed to determine the ferric oxide and alumina, lime and magnesia, as directed on page 521.

The Determination of Alkalies, Sulphuric Acid, Carbon Dioxide Combined Water and Loss on Ignition

For the determination of these constituents refer to the methods given under cement. Use the fusion method for sulphur and employ only ½ gram for a sample in determining carbon dioxide.

RAPID DETERMINATION OF LIME AND MAGNESIA

S. B. Newberry[1] suggests the following rapid scheme for determining lime and magnesia in limestone, etc. "Prepare N/5 hydrochloric acid and N/5 caustic soda solutions, and standardize with pure, transparent Iceland spar. One-half gram of spar should exactly neutralize 50 cc. of acid.

"Weigh out ½ gram of finely ground limestone, transfer to an Erlenmeyer flask of about 500 cc. capacity, provided with rubber stopper and thin glass tube about 30 inches long to serve as a condenser, as described on page 236. Run into the flask 60 cc. N/5 acid; attach the condenser and boil gently, allowing no steam to escape from the tube, for about two minutes. Wash down the tube into the flask with a few cc. of water from wash-bottle; remove the condenser and *cool the solution thoroughly* by immersing the bottom of the flask in cold water. When quite cold, add five drops of phenolphthalein solution, (1 gram in 200 cc. alcohol), and titrate back to first pink color with N/5 soda solution. It is important to recognize the point at which a faint pink color first appears throughout the solution, even though this may fade out in a few seconds. If alkali be added to a permanent and strong red color, the lime will come too low. Let us call the amount of acid used the *first acid*, and the alkali used to titrate back the *first alkali*.

"Transfer the neutral solution to a large test-tube, 12 inches long and 1 inch inside diameter, marked (with a paper strip or otherwise) at 100 cc. Heat to boiling, and add N/5 soda solution, about 1 cc. at a time, boiling for a moment after each addition, till a deep red color, which does not become paler on boiling, is obtained. This point can be easily recognized within one-half cc. after a little practice. Note the number of cc. soda solution added to the neutral solution, as *second alkali*. Dilute to 100 cc., boil for a moment and set the tube aside to allow the precipitate to settle. When settled, take out 50 cc. of the clear solution by means of a pipette, and titrate back to colorless with N/5 acid. Multiply by 2 the number of cc. acid required to neutralize, and note as *second acid*.

[1] *Cement and Engineering News*, March, 1903, p. 35.

"The calculation is as follows:

Second alkali — second acid, $\times$ 2 $\times$ 0.40 = % MgO.

First acid — (first alkali + second alkali — second acid), $\times$ 2 $\times$ 0.56 = % CaO.

"Example: To ½ gram limestone were added 60.00 cc. acid, (*first acid*). To titrate back to first pink, 11.60 cc. alkali were required, (*first alkali*). The solution was then transferred to test-tube, boiled, and 3.55 alkali added to permanent deep red color, (*second alkali*). After diluting to 100 cc. and settling, 50 cc. of the red solution required 0.45 cc. acid to decolorize it, (0.45 $\times$ 2 = 0.90 = *second acid*).

3.55 — 0.90, $\times$ 2 $\times$ 0.40 = 2.12 % MgO.

60.00 — (11.60 + 3.55 — 0.90) $\times$ 2 $\times$ 0.56 = 51.24 % CaO."

NOTES

"Nitric acid may be used in place of hydrochloric; the latter appears, however, to give slightly better results.

"Not more than 1 cc. excess of alkali should be added in precipitating the magnesia; the 'second' should therefore not exceed 1. Larger excess of alkali tends to throw down lime.

"The settling usually requires only a few minutes, unless much magnesia is present; it may be greatly hastened by allowing the test-tube to stand two or three minutes, then immersing the lower part for a moment in cold water.

"If results are desired in percentages of magnesium carbonate and calcium carbonate the factors 0.84 and 1.00 are to be substituted for 0.40 and 0.56, respectively.

"The tendency of the method is to give slightly too high results on magnesia and too low results on lime. This is partly due to the formation of calcium carbonate, by the action of the carbon dioxide of the air, during the precipitation of the magnesia. By the use of a large test-tube, as above described, this error is so far reduced as to be insignificant. Another source of shortage of lime is to be found in the presence, in certain materials, of small proportions of lime in a form insoluble in dilute acid."

In determining lime in cement-rock or in cement mixtures made from clay containing calcium silicates this method always gives low results for the above reason. To use the method on such material it is necessary to determine a "correction factor" by comparison between the lime found by this method and that on page 523, in a series of standard samples. By subtracting the lower from the higher results, a constant is obtained which is to be added to all results obtained by titration with the acid and alkali.

Modification by Brandenburg and Avakian

Messrs. Brandenburg and Avakian, of the Cowell Portland Cement Co., modify Newberry's method as follows: Prepare 2/5 N acid (HCl) and alkali (NaOH) solutions adding 2 cc. of a 1 per cent solution of phenolphthalein to each liter of standard acid. Standardize against Iceland spar as usual. Weigh 1 gram of the sample into a 300 cc. Erlenmeyer flask and add 60 cc. of the standard acid. Attach to the condenser described on page 514 and boil two or three minutes. Instead of titrating hot as in ordinary acid and alkali determinations of lime, *cool* the solution under the tap and when cold titrate rapidly, yet carefully, with the 2/5 N alkali until the first pink color is obtained and record the number of cc. of alkali so used as "A."

Attach flask to the condenser again and heat just to boiling, having ready 1.5 grams of solid sodium oxalate. Add the latter to the solution in the flask and boil for a minute or two. Remove the flask from the condenser and flame and add to the solution a decided and measured excess of 2/5 N alkali. Record the number of cc. of alkali so used as "B."

Attach flask to condenser, boil the contents for two or three minutes, remove from the flame, cool under the tap, transfer contents to a 200 cc. graduate, fill to the mark with water and shake thoroughly. Filter through double filter-paper into a 100 cc. graduate, discarding the first and probably turbid filtrate. Filter off 100 cc., transfer to a clean Erlenmeyer flask and titrate carefully back with the 2/5 N acid. Note the number of cc. of acid so used, double this reading and record as "C."

The results are calculated as follows:

$CaCO_3 = 60 - (A + B - C) \times \text{factor}.$

$MgCO_3 = (B - C) \times \text{factor}.$

For Example: If 60 cc. of 2/5 N acid are used to dissolve the sample, 9.85 cc. of alkali to back titrate (A), 40.0 cc. to precipitate the magnesia (B) and 31.7 to back titrate C; then

$$CaCO_3 = 60 - (9.85 + 40 - 31.7) \times 2 =$$
$$41.85 \times 2 = 83.70\ \%.$$

$MgCO_3 = (40 - 31.7) \times 1.69 = 8.3 \times 1.69 = 14.03\ \%$.

The above example assumes acid and alkali are exactly 2/5 N strength.

NOTES

The titration of the solution with alkali should not be continued after the "first pink" is reached, even though the color fades. Any additional alkali after the "first pink" will be consumed for precipitation of the magnesia.

The object of the addition of oxalate, according to the authors, is to form calcium oxalate and thus render the excess alkali added later inactive and remedy the error in the older method due to the precipitation of the calcium by the alkali. Should magnesia be precipitated by the oxalate no error will occur as the magnesium oxalate is converted to the hydrate by the excess alkali later employed.

METHODS FOR CLAY AND SHALE

Finely grind the sample of clay and heat at 100° to 110° C. for one hour in an air-bath. Transfer 1 gram of the dried clay to a fairly large platinum crucible. Mix with it by stirring with a smooth glass rod 10 grams of sodium carbonate and a little sodium nitrate. Heat over a Bunsen burner, gently at first, for a few minutes and then to quiet fusion over a blast-lamp. Run the fused mass well up on the sides of the crucible and allow to cool. Nearly fill the crucible with hot water and set on the hot-plate for a few minutes. Pour the solution and as much of the mass as has become detached from the crucible into a casserole or better a platinum dish. Repeat this treatment until the mass has become thoroughly disintegrated. Treat what remains in the crucible with dilute hydrochloric acid and pour the acid into the casserole or dish. Clean out the crucible with a rubber-tipped rod and after acidifying with hydrochloric acid evaporate the contents of the casserole to dryness. Proceed as in *A* or *B*. *A* is the shorter method but *B* is the more reliable.

A. Heat in an air-bath at 110° C. for one hour, or until all odor of hydrochloric acid has vanished. Cool, moisten the mass with dilute hydrochloric acid, add a little water and again evaporate to dryness. Now add 30 cc. of dilute hydrochloric acid, digest at a gentle heat for a few moments and add 100 to 150 cc. of hot water. Allow to stand a few minutes on the hot-plate and filter.

Wash the residue thoroughly with hot water, ignite over a Bunsen burner until all carbon is burned off, and then for five minutes over a blast-lamp, and weigh as SiO_2.

B. The residue, without further heating, is treated at first with 10 cc. of dilute HCl. The dish is then covered and digestion allowed to go on for ten minutes on the bath, after which the solution is diluted slightly, filtered, and the separated silica washed thoroughly with hot water. The filtrate is again evaporated to dryness, the residue, without further heating, taken up with acid and water, and the small amount of silica it contains separated on another filter-paper. The two papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for fifteen minutes. The precipitate is then weighed as SiO_2. This precipitate is more or less contaminated by iron oxide and alumina. In accurate work the amount of these must be determined in the following manner and deducted from the weight of SiO_2 as found above. Moisten the weighed silica with a few drops of dilute sulphuric acid and half fill the crucible with hydrofluoric acid. Evaporate to dryness by placing over a burner in an inclined position so that the low flame plays upon the side of the crucible and the evaporation takes place only from the surface. Ignite and weigh. The difference between the two weights is the silica, SiO_2.

Ferric Oxide and Alumina

Add a few drops of bromine water and heat the filtrate from the silica, which should measure about 150 cc., to boiling, and add ammonia in slight but distinct excess; boil for a few moments and allow the precipitate to settle. Filter and wash several times with hot water. Remove the filtrate from under the funnel and dissolve the precipitate of iron and alumina in a mixture of 15 cc. of dilute nitric acid and 15 cc. of cold water, by pouring back and forth through the filter as long as any precipitate remains. Wash the filter-paper well with cold water, dry, place in the weighed platinum crucible containing the residue from the purification of the silica if this has been done, and set aside. Reprecipitate the iron and alumina in the filtrate as before by adding a

slight but distinct excess of ammonia, filter, and wash once with hot water. Place in the crucible with the other paper and ignite, using the blast as in determining silica and weigh as

$$Fe_2O_3 + Al_2O_3(TiO_2 + P_2O_5 + Mn_3O_4).$$

Determine the ferric oxide in the precipitate as in *A*, *B* or *C* below and subtract the amount from this weight; the difference will be the $Al_2O_3(TiO_2 + P_2O_5 + Mn_3O_4)$.

A. Fuse the ignited precipitate with sodium carbonate, treat the fused mass with hot water and wash it out into a small beaker, allow the residue to settle and decant off the clear supernatant liquid through a small filter, leaving the residue in the bottom of the beaker. Wash the filter-paper once and pour a little hot concentrated hydrochloric acid through the filter into the beaker containing the residue. Heat gently, but do not boil. When all the residue is dissolved, determine the iron in the solution by reduction with stannic chloride and titration with potassium bichromate as directed on page 463.

B. The precipitate is fused with 3 or 4 grams of potassium bisulphate at a very low temperature and the melt is dissolved in water acidified with sulphuric acid. The solution is then reduced with zinc or hydrogen sulphide, (preferably the latter since clays sometimes contain considerable titantic oxide), and the iron determined as directed on page 459.

C. Weigh out a fresh sample of ½ gram. Mix intimately with 2 grams of precipitated calcium carbonate and 2 grams of sodium carbonate. Ignite for fifteen minutes in a large platinum crucible over a good blast-lamp. Cool the mass and dissolve in dilute hydrochloric acid. If much silica separates out evaporate to dryness and filter. Otherwise add ammonia in excess to the solution, filter off the precipitated Fe_2O_3, dissolve the latter in an excess of hydrochloric acid, and determine the iron as directed on page 463 or dissolve in sulphuric acid and determine as directed on page 459.

Lime

Heat the filtrate from the iron and alumina to boiling and add an excess of a saturated solution of ammonium oxalate. Stir and boil for a few minutes and set aside for several hours to allow

the complete precipitation of the lime. Filter, wash, dry, and ignite over a blast-lamp until the weight is constant. Weigh as calcium oxide, CaO. Or determine volumetrically with permanganate as described on page 455.

Magnesia

To the filtrate from the calcium oxalate add sufficient hydrochloric acid to make it slighly acid and then 30 cc. of sodium phosphate solution. Concentrate the solution to about 200 cc. by evaporation and cool. Then add ammonia drop by drop, with constant stirring until the liquid is slightly ammoniacal and the precipitate begins to form. Stop adding ammonia and stir for five minutes, then add one-tenth the volume of the liquid of strong ammonia and continue the stirring for five minutes more. Allow the solution to stand in a cool place over night, filter, wash with a mixture of 1,000 cc. water, 500 cc. ammonia (sp. gr. 0.96), and 150 grams ammonium nitrate. Dry, ignite (do not use the blast-lamp), and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Multiply this by 0.36219 for magnesium oxide, MgO.

NOTES

Clay is practically unacted upon by hydrochloric acid and requires fusion with alkaline carbonates for its decomposition.

Should the solution, on evaporation to dryness, show a tendency to climb the sides of the dish, greasing the latter lightly with vaseline or paraffine will remove the difficulty.

The amounts of lime and magnesia in clays are small, so that the filtrate and washings from the second ammonia precipitation of the iron and alumina may be rejected and the lime and magnesia determined in the first filtrate only. For the same reason it is unnecessary to reprecipitate the calcium oxalate, although the solution is largely contaminated by sodium salts from the alkaline fusion.

Determination of the Alkalies

To determine the alkalies use 1 gram of the clay, 1 gram of ammonium chloride and 8 grams of calcium carbonate and proceed as directed for determining the alkalies in cement on page 486.

Determination of Free, Hydrated and Combined Silica[1]

To ascertain how much of the silica found exists in combination with the bases of the clay, how much as hydrated acid, and how much

[1] Cairns' Quantitative Chemical Analysis, page 68.

as quartz sand or as a silicate present in the form of sand, proceed as follows.[2]

Let A represent silica in combination with the bases of the clay.

Let B represent hydrated silicic acid.

Let C represent quartz sand and silicates in the form of sand, *e. g.*, feldspar sand.

Dry 2 grams of the clay at a temperature of 100° C., heat with sulphuric acid, to which a little water has been added, for eight or ten hours, evaporate to dryness, cool, add water, filter out the undissolved residue, wash, dry, and weigh (A + B + C). Then treat it with sodium carbonate. Transfer it, in small portions at a time, to a boiling solution of sodium carbonate contained in a platinum dish, boil for some time and filter off each time, still very hot. When all is transferred to the dish, boil repeatedly with strong solution of sodium carbonate until a few drops of the liquid finally passed through the filter remain clear on warming with ammonium chloride. Wash the residue, first with hot water, then (to insure the removal of every trace of sodium carbonate which may still adhere to it) with water slightly acidified with hydrochloric acid, and finally with water. This will dissolve (A + B) and leave a residue (C) of sand, which dry, ignite, and weigh.

To determine (B), boil 4 or 5 grams of clay (previously dried at 100° C.) directly with strong solution of sodium carbonate in a platinum dish as above, filter and wash thoroughly with hot water. Acidify the filtrate with hydrochloric acid, evaporate to dryness, and determine the silica as usual. It represents (B) or the hydrated silicic acid.

Add together the weights of (B) and (C), thus found, and subtract the sum from the weight of the first residue (A + B + C). The difference will be the weight of (A) or the silica in combination with the bases of the clay.

If the weight of (A + B + C) found here to be the same as that of the silica found by fusion in a similar quantity in the analysis of the clay, the sand is quartz, then the sand contains silicates.

The weight of the bases combined with silica to form silicates can be found by subtracting the weight of total silica found in 1 gram in the regular analysis, from the weight (A + B + C) in 1 gram.

NOTES

The following scheme is much less trouble than that described above and gives the silica present as sand and silicates undecomposable by sulphuric acid and that in combination with the alumina or combined silica.

Heat 1.25 grams of the *finely* ground and dried (at 100° C.) clay with 15 cc. of concentrated sulphuric acid to near the boiling-point of the acid and digest for from ten to twelve hours at this temperature.

[2] Compare Fresenius' Quantitative Analysis, 5th Ed., 1865, Sec. 236.

Cool, dilute and filter. Wash and ignite the residue to a constant weight. Call this weight A. After weighing brush the residue which consists of silica present as sand and undecomposable silicates and silica from the decomposition of the silicates of alumina, into an agate mortar, grind very finely and weigh 0.5 gram of it into a platinum dish containing 50 cc. of *boiling* caustic potash solution (of 1.125 sp. gr.). Boil for five minutes, filter, wash, first with hot water and then with water containing a little dilute hydrochloric acid and then again with hot water, dry and ignite to a constant weight. Call this weight B. Multiply A by 0.4 (to correct the 1.25 grams of clay used to correspond to the 0.5 gram of the residue taken for treatment with caustic potash solution) and subtract B from the product. Multiply the difference by 200 for the per cent of silica combined with alumina in the clay. This deducted from the total silica found by analysis gives the silica as sand and undecomposable silicates.

Determination of Coarse Sand

In examining clay to be used for cement manufacture, it is not so important to know the chemical condition in which the silica exists as its physical state, *i. e.*, whether the sand grains are large or small. Pure quartz sand if sufficiently finely powdered will combine with lime at the temperature of the rotary kiln, so that what is more requisite in clay to be used for cement manufacture is that the sand shall be present in fine grains. To test the clay, along this line, weigh 100 grams of clay into a beaker and wet with water. Triturate to a thin slip with a glass rod and wash into a No. 100 test sieve. Now place the sieve under the tap and wash as much of the clay as possible through the meshes of the sieve with a gentle stream of water. Dry the sieve on a hot-plate and brush out the dry residue failing to pass through it on to the balance pan and weigh. The weight in grams gives the percentage of the clay failing to pass a No. 100 sieve. The clay may also be tested in a similar manner on the No. 200 sieve and the residues may be subjected to chemical analysis.

Marls are examined by the same method to determine fineness.

Determination of Water of Combination

Should the clay contain very little organic matter, iron pyrites or calcium carbonate, heat 1 gram of the previously dried cement for twenty minutes to a bright redness over a Bunsen burner.

The loss in weight will represent the water of combination. If, however, the clay contains much organic matter, calcium carbonate or iron pyrites, the water of combination should be determined by absorption in a weighed calcium chloride tube as described for cement analysis on page 475.

Many chemists simply heat 1 gram of dried clay over a blast for twenty minutes reporting the loss of weight as *loss on ignition*. This loss, of course, comes from combined water and carbon dioxide driven off (from the decomposition of carbonates), organic matter burned and iron pyrites changed from iron sulphide, FeS_2, to ferric oxide.

Sulphur and Iron Pyrites

For the determination of sulphur in clay, proceed as directed for determining this constituent in cements by fusion with sodium carbonate and potassium nitrate. Multiply the weight of barium sulphate by 0.25701 and report as iron pyrites, FeS_2, or by 0.13738 and report as sulphur. If reported as FeS_2 multiply the percentage of this latter by 0.90836 and deduct from the Fe_2O_3.

Rapid Determination of Silica, Iron Oxide and Alumina

Weigh 0.5 gram of the finely ground sample of clay into a platinum crucible and mix with it intimately, by stirring with a glass rod rounded at the ends, 1 gram of precipitated calcium carbonate such as is used for alkali determination and ½ gram of finely powdered dry sodium carbonate. The mixing must be thorough. Brush off the rod into the crucible with a camel's hair brush and place the covered crucible over a Bunsen burner turned low. Gradually raise the flame till the full heat is attained, keep at this temperature for two or three minutes, and then remove to the blast-lamp and ignite strongly for five minutes. Cool the crucible by plunging its bottom in cold water and place it on its side in a platinum or porcelain dish or casserole. Add 10 cc. of water and 10 cc. of dilute (1 : 1) acid. As soon as the mass is dissolved out of the crucible remove the latter, rinse it off into the dish removing any solid particles with a policeman and evaporate the solution to dryness. Heat the dish at 120° C. until all

odor of acid has disappeared. Cool, add 20 cc. of hydrochloric acid (1:1), cover and boil a few minutes, add 50 cc. of water, boil a few minutes longer, filter, wash and ignite, first over the burner, until carbon is all burned off, and then over the blast for ten minutes. Cool and weigh as silica, SiO_2.

Iron Oxide and Alumina

Heat the filtrate to boiling, after adding a few drops of bromine water, add ammonia in slight but distinct excess and again heat to boiling. Continue boiling for two or three minutes and after allowing the precipitate to settle, filter and wash once with hot water. Invert the funnel over the beaker in which the precipitation was made and wash the precipitate back into this with a stream of hot water from a wash-bottle. Dissolve in dilute nitric acid, heat to boiling and reprecipitate with ammonia. Boil for a few minutes, allow the precipitate to settle, and filter. Wash once with hot water, ignite (using the blast finally) and weigh as oxides of alumina and iron, $Al_2O_3 + Fe_2O_3$.

METHODS FOR GYPSUM OR PLASTER OF PARIS

Determination of Silica, Iron Oxide, Alumina, Lime and Magnesia

Weigh 0.5 gram of the finely ground sample into a platinum dish or porcelain casserole and add 20 cc. of dilute hydrochloric acid (1:1). Evaporate to dryness and heat the residue, at 110° C. until all odor of hydrochloric acid has vanished from the contents of the dish. Cool and add 10 cc. of dilute hydrochloric acid, cover with a watch-glass and heat for five minutes. Dilute to 50 cc. and heat a little longer. Filter, wash the precipitate well with hot water, ignite and weigh. Report as insoluble silicious matter or proceed as follows: Ignite 0.5 gram of the sample with ½ gram of pulverized sodium carbonate first over a burner and then over a blast. Place the crucible in a dish or beaker and dissolve out the mass in a little dilute hydrochloric acid. Evaporate the solution to dryness and heat, at 110° C., until all odor of hydrochloric acid has disappeared from the dry mass. Dissolve in a

little hydrochloric acid and water, as before, filter, wash, ignite and weigh as SiO_2.

Heat the filtrate from the SiO_2 or that from the "insoluble silicious matter," as the case may be, to boiling, precipitate the iron and aluminum as oxides with ammonia and proceed as in the analysis of cements on page 441.

Determination of Sulphuric Acid

Weigh 0.25 gram of the finely ground sample into a beaker and dissolve in 5 cc. of dilute (1 : 1) hydrochloric acid, by the aid of heat. Dilute to 100 cc. with hot water. Digest for a few minutes and filter. Wash the paper and residue thoroughly, with hot water, until the filtrate measures about 250 cc. Heat this latter to boiling and add, with constant stirring, 20 cc. of barium chloride solution, also boiling hot, and stir for five minutes. Remove from the source of heat and allow to stand over night in a warm place. In the morning, filter through a double filter-paper or a "Shimer filter tube"[1] and wash well with hot water. Ignite (without using the blast) and weigh as $BaSO_4$. This weight multiplied by 0.34300 gives the SO_3 in the sample or by 0.62184 the $(CaSO_4)\ H_2O$ or by 0.7375 the $CaSO_4.2H_2O$. Do not forget a quarter gram sample has been taken.

The above method is that generally employed. The writer, however, prefers to separate the lime from the solution before precipitating the sulphur. His method is as follows:—Weigh 0.25 gram of the sample into a small beaker and add 5 cc. of dilute (1 : 1) hydrochloric acid. Heat until solution is complete. Dilute to 100 cc. make alkaline with ammonia and add an excess of ammonium carbonate solution. Boil for a few minutes and filter. Wash the residue with hot water and redissolve in 5 cc. of acid. Again neutralize with ammonia and add ammonium carbonate solution. Filter and wash the residue with hot water a few times. Combine the filtrates from the two precipitations. Acidify with hydrochloric acid, using an excess of about 3 or 4 cc. Heat to boiling and precipitate the sulphur as directed above with barium chloride.

[1] See page 472.

Determination of Water

Weigh 1 gram of the finely ground sample in a weighed platinum crucible and heat[1] for one hour at 100-105° C. Cool and weigh. The loss in weight represents the "moisture" or "water below 105° C."

Determine the combined water and carbon dioxide as directed for cement on page 475, or:

Place the crucible over a Bunsen burner and heat at a *low* red temperature for thirty minutes. The loss in weight represents "water of combination" or "water above 105° C." If the heating has been too high, some sulphuric acid will have also been lost. To check this, dissolve the sample out of the crucible, after ignition, with hydrochloric acid. Dilute to about 100 cc. and filter into a 200 cc. flask. Wash well with hot water and dilute with water to the mark. Measure of this volume 50 cc. dilute to 250 cc. and determine the SO_3 as directed previously. If loss has occurred, this determination will give a lower figure than the other. In this case deduct the difference between the percentages found by the two trials from percentage of loss in weight over the burner for the percentage of water of combination. If the heating of the crucible over the Bunsen burner has been done at a heat not higher than cherry-red there should be no loss of sulphuric acid, however.

Determination of Carbon Dioxide

Determine carbon dioxide as directed on page 483, for cement, using the evolution method.

[1] See page 485.

PHYSICAL TESTING

CHAPTER XIX

INSPECTION OF CEMENT

Standard Specifications and Tests for Portland Cement[1]

1.[2] *Definition.*—Portland cement is the product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum.

I. Chemical Properties

2. *Chemical Limits.*—The following limits shall not be exceeded:

Loss on ignition, per cent	4.00
Insoluble residue, per cent	0.85
Sulfuric anhydride (SO_3), per cent	2.00
Magnesia (MgO), per cent	5.00

II. Physical Properties

3. *Specific Gravity.*—The specific gravity of cement shall be not less than 3.10 (3.07 for white Portland cement). Should the test of cement as received fall below this requirement a second test may be made upon an ignited sample. The specific gravity test will not be made unless specifically ordered.

4. *Fineness.*—The residue on a standard No. 200 sieve shall not exceed 22 per cent by weight.

[1] These specifications were approved March 31, 1922, as "American Standard" by the American Engineering Standard Committee.

[2] Where numbers occur in front of paragraphs, these appear in the Standard specifications, the original numbering being retained to facilitate references.

5. *Soundness.*—A pat of neat cement shall remain firm and hard, and show no signs of distortion, cracking, checking, or disintegration in the steam test for soundness.

6. *Time of Setting.*—The cement shall not develop initial set in less than forty-five minutes when the Vicat needle is used or sixty minutes when the Gillmore needle is used. Final set shall be attained within ten hours.

7. *Tensile Strength.*—The average tensile strength in pounds per square inch of not less than three standard mortar briquettes (see Section 50[1]) composed of one part cement and three parts standard sand, by weight, shall be equal to or higher than the following:

Age at test, days	Storage of briquettes	Tensile strength, lb. per sq. in.
7	1 day in moist air, 6 days in water	200
28	1 day in moist air, 27 days in water	300

8. The average tensile strength of standard mortar at twenty-eight days shall be higher than the strength at seven days.

Standard Specifications for Packages, Marking and Storage

9. *Packages and Marking.*—The cement shall be delivered in suitable bags or barrels with the brand and name of the manufacturer plainly marked thereon, unless shipped in bulk. A bag shall contain 94 pounds net. A barrel shall contain 376 pounds net.

10. *Storage.*—The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment, and in a suitable weather-tight building which will protect the cement from dampness.

Standard Specifications for Inspection and Rejection

11. *Inspection.*—Every facility shall be provided the purchaser for careful sampling and inspection at either the mill

[1] See page 640.

or at the site of the work, as may be specified by the purchaser. At least ten days from the time of sampling shall be allowed for the completion of the seven-day test, and at least thirty-one days shall be allowed for the completion of the twenty-eight-day test. The cement shall be tested in accordance with the methods hereinafter prescribed. The twenty-eight-day test shall be waived only when specifically so ordered.

12. *Rejection.*—The cement may be rejected if it fails to meet any of the requirements of these specifications.

13. Cement shall not be rejected on account of failure to meet the fineness requirement if upon retest after drying at 100° C. for one hour it meets this requirement.

14. Cement failing to meet the test for soundness in steam may be accepted if it passes a retest using a new sample at any time within twenty-eight days thereafter.

15. Packages varying more than 5 per cent from the specified weight may be rejected; and if the average weight of packages in any shipment, as shown by weighing fifty packages taken at random, is less than that specified, the entire shipment may be rejected.

Methods of Inspection

It is now the custom to test carefully all cement to be used upon important work. Most of the large cities of the country maintain well equipped laboratories and systematically inspect all cement used upon the various municipal works undertaken by them. The Bureau of Standards in Washington tests all cement used by the national government in fortifications, dry-docks, public buildings, etc. Various private laboratories also make a specialty of inspecting the cement to be used in big buildings, reservoirs, retaining walls, etc., for private corporations, while the railroads, most of them, have well equipped laboratories for testing such materials, cement among them, as they purchase.

Cement may be inspected either at the mill before shipment, or at the place where it is to be used, after receipt. The actual tests, of course, may be made at either of these points, or the samples can be properly labelled and sent some distance to a convenient

laboratory. The New York Rapid Transit Railroad (Subway) Commission pursued the former of these two plans and inspected the cement at the mill itself. The Philadelphia Rapid Transit Company, on the other hand, followed the latter plan and inspected the cement as received in Philadelphia. Both plans can be made to give entire satisfaction.

Where the product of one mill alone is to be used for the work, the testing laboratory may be located at the mill from which the cement is supplied. Otherwise, it should, of course, be located at some convenient point to which samples can readily be sent.

The suggestion has been made that the cement companies furnish the inspector testing appliances, quarters, etc., for doing this work. This seems to be asking rather much of the manufacturers, as their laboratories are, most of them, already overcrowded and the presence of an outsider, in the one part of the plant where trade secrets are likely to be exposed, is not desirable.

Inspection at the Mill

Where cement inspection is done at the mill certain bins are set aside by the proper authority at the cement mill, and the spouts leading into these are closed by means of a wire and lead seal such as is used in closing box cars; the idea of sealing the spouts is to prevent the bins from being emptied and refilled without the knowledge of the inspector. Any method which will insure against this, such as sealing wax and string will answer as well as the lead seal and wire. In some cases, it may be sufficient to rely upon the honesty of the mill authorities and to merely accept their word or promise that the bin has not been tampered with. Or an affidavit may be secured from the stock-house foreman to this effect.

After selecting the bin and insuring against its being emptied and refilled, it must be carefully sampled. How this is to be done will depend somewhat upon the size and shape of the bin. Since cement when freshly ground and hot flows not unlike a liquid, the cement first run into the bin will be almost all of it deposited in a layer on the floor of the bin. For this reason, the

means used for sampling the bin must be such that the cement at the bottom of the bin is included in the sample. One page 548, a rod suitable for sampling shallow bins is described. This is probably as satisfactory as any sampling device can well be, provided the bins are not too deep. The taking of a sample from the floor of a bin may necessitate the use of a sledge hammer to drive the rod through the mass of cement in the bin. If the inspector is permanently located at the mill, the sample can be taken easiest, when the bin is being filled, by means of an automatic sampler such as is described on page 496.

The importance of sampling the floor of a bin will be understood, when it is known that, in a bin of unsound cement, a sample taken only a few days after the bin has been filled and representing only the surface layer of cement will often be sound, while one representing the bottom layer may be unsound after even a month's seasoning.

A shallow rectangular bin should be sampled in at least four places—the four corners—and may be sampled in as many more as the inspector sees fit. A sample drawn from the four corners of shallow bins, filled by a spout in the middle, will be representative. The feet and legs of the man taking the sample may be protected as he walks over the surface of the cement by thrusting them in clean new cloth cement bags (a few of which can be found around all mills) and tying them securely around the legs above the knee. The cement sample should be placed in clean cloth bags, which should be properly closed and sealed and expressed or conveyed to the testing laboratory. If the inspecting laboratory is located at the mill, paper bags or tin buckets may be used for this purpose. Small milk cans holding about 2 quarts will be found excellent for transporting samples, as the tops can be wired down tight and the samples are protected from changes due to exposure to air in them.

The objection has been raised to the use of cloth bags, that an unsound cement would probably be seasoned sound after a two or three days' journey in them and some inspectors use tin buckets or cans, with tightly fitting covers for this purpose. On the other hand, if an unsound sample is made sound by exposure in

cloth bags after a few days' journey by express, the inspector may rest assured that the body of the bin will be seasoned equally well by an equally long journey by freight in a box car. Also cement occasionally leaves the mill "slow-setting" and arrives at the work "quick-setting," so that shipment of a sample in cloth should give a line on the likelihood of the main body of the cement doing this.

When the sample arrives at the testing laboratory, its receipt is properly recorded together with such data as the brand, manufacturer, bin, date sampled, etc., after which, to readily identify briquettes, etc., it is given a running number. The sample is then carefully mixed, and a sufficient quantity of this for the necessary tests is taken and passed through a 20-mesh sieve to remove lumps, after which it is submitted to the tests called for by the specifications. The large sample is then stored away in a tin can or a fruit jar for future reference, retests, etc.

When the results of the tests are at hand, the laboratory notifies its agent at the mill, who in turn informs the authorities of the cement company that such and such a bin is ready for shipment, and when cement is needed it is also the duty of the mill inspector to see that the cement is packed from accepted bins and accepted bins only.

This system usually necessitates the holding of a bin for from five to six weeks, if the specifications call for a twenty-eight-day test, or about two weeks if only the seven-day test is relied upon. This often puts the manufacturer to much inconvenience and trouble, but, from the standpoint of the consumer, seems to be preferable. On the other hand the manufacturer has the satisfaction of knowing that, after the cement is once shipped, it is off his hands for good and all with no chance for complaint from the purchaser.

Another form of inspection at the mill consists in sampling the cars as they are filled. This is usually done by taking a small quantity of cement from one in every forty bags packed. These small samples are then either mixed or not as desired and sent to the laboratory for tests. (See directions for sampling, page 546). The car is not held for the result of these but is

immediately billed to its destination. By the time it has reached this, the seven-day tests will usually have been completed. If the tests are satisfactory the car can be immediately unloaded and used. This method is employed by most testing laboratories.

Inspection on the Work

When the cement is inspected as it arrives at the work, the cars are unloaded and sampled—one bag out of every forty (or one barrel in ten) being selected and a sample drawn from it as indicated on page 547. These samples may be either mixed or kept separate in clean paper bags. The contents of each car should be piled in such a way that it may be kept to itself and marked by a properly tagged board or sign. When the work permits the use of a large store house, this should be divided into bins holding a carload, 200 barrels or 1,000 bags. The cement should be held in storage until the results of the tests are known when, if these are satisfactory, the contractor or foreman may be notified that he can use the cement from such and such a pile or bin.

When a car of cement fails to pass the specifications, the manufacturer is usually notified at once that such cement has been found unsatisfactory. He will then probably ask for a retest, which should be made from new samples, drawn in the presence of his representatives, and, if possible, the tests also should be repeated in the presence of this representative. If this latter can not be done, the sample should be divided into three parts and placed in tin cans or fruit jars and closed up tight. One of these samples should be tested by the manufacturer and, unless his results agree with those of the consumer, the third sample should be sent to some reliable, competent third party with the agreement of both manufacturer and consumer to stand by his results.

Should the cement finally be found unsatisfactory, it is usually returned to the manufacturer, who replaces it with another consignment or else it is used on some unimportant part of the job. Unsound cement may be held until it has been seasoned sound and quick-setting cement may often be made slow-setting by a small addition (0.5 per cent) of plaster or slaked lime. In both

instances, the resulting concrete will be satisfactory and the manufacturer will usually be willing to bear the expense of storage, or addition of plaster or lime, rather than pay the double freight, necessary to its replacement with other cement.

When the cement supplied by a manufacturer habitually fails to pass the specifications under which it is sold, he deserves little consideration from the engineer or inspector, but, when the failure of a brand to meet specifications is a rare incident, the engineer can afford to be lenient, if his work is not endangered thereby, especially if the average quality of the cement is far above that asked for by him, in his specifications.

Standard Methods of Sampling

The methods of sampling recommended by the standard specifications are as follows:

16. *Number of Samples.*—Tests may be made on individual or composite samples as may be ordered. Each test sample should weigh at least 8 pounds.

17. (*a*) *Individual Sample.*—If sampled in cars one test sample shall be taken from each 50 barrels or fraction thereof. If sampled in bins one sample shall be taken from each 100 barrels.

(*b*) *Composite Sample.*—If sampled in cars one sample shall be taken from one sack in each forty sacks (or 1 barrel in each 10 barrels) and combined to form one test sample. If sampled in bins or warehouses one test sample shall represent not more than 200 barrels.

18. *Method of Sampling.*—Cement may be sampled at the mill by any of the following methods that may be practicable, as ordered:

(*a*) *From the Conveyor Delivering to the Bin.*—At least 8 pounds of cement shall be taken from approximately each 100 barrels passing over the conveyor.

(*b*) *From Filled Bins by Means of Proper Sampling Tubes.*—Tubes inserted vertically may be used for sampling cement to a maximum depth of 10 feet. Tubes inserted horizontally may

be used where the construction of the bin permits. Samples shall be taken from points well distributed over the face of the bin.

(*c*) *From Filled Bins at Points of Discharge.*—Sufficient cement shall be drawn from the discharge openings to obtain samples representative of the cement contained in the bin, as determined by the appearance at the discharge openings of indicators placed on the surface of the cement directly above these openings before drawing of the cement is started.

19. *Treatment of Sample.*—Samples preferably shall be shipped and stored in air-tight containers. Samples shall be passed through a sieve having 20 meshes per linear inch in order to thoroughly mix the sample, break up lumps and remove foreign materials.

The knowledge usually sought by a test and analysis of cement is the average composition and properties of a given lot or bin. In order that it shall give this, it is necessary that the small sample used in the tests shall fairly represent the whole quantity, possibly many tons. In a large lot of cement, it often happens that a small sample, or even a large sample, taken from one place in the bin or one barrel in the consignment, will not represent the cement, since this particular point in the bin, or this special barrel, might be better or worse than the remainder, hence the directions to take at least twenty samples in a car of 200 barrels, or to sample at frequent places in a bin.

Samplers

Practically all cement in the United States is now packed in Bates Valve bags, the sampling from which is easy. This is usually done by means of a small brass tube from 18 to 20 inches long, both ends of which are left open but one end of which is bevelled at an angle of about 45°. This tube is simply thrust into the bag through the valve of the latter and the cement which it retains is withdrawn for the sample. The tube should be thrust into the bag from valve to center not across the end of the bag.

In sampling cement from a barrel a small brass tube with a slit cut down the middle may be used. The slit is neces-

sary as the cement becomes packed in the tube when it is thrust into the cement and it is necessary to run a lead pencil or nail up and down the opening to get the cement out. The tube for this purpose need not be over two feet long and its upper end should be screwed into a T, the latter forming a handle. The forms of grain and sugar samplers sold by dealers in apparatus for cement testing may be used for sampling bags and barrels.

In sampling cement packed in Bates valve bags, this can be done without untying the bags by thrusting a brass tube into the

Fig. 157.—Jointed Rod for Sampling Stock House Bins.

contents of the bag through the valve. The spill from the tube of this machine will also make a good average sample of bags as packed.

For sampling bins of cement in the stock houses at the mill the depth of the former, often eight or more feet, makes their proper sampling a difficult matter unless a specially devised sampling rod is at hand. In order to get an average of the bin it is necessary to draw portions from it at all depths and at both ends. An excellent apparatus for doing this, consists of a long iron rod such as is shown in Fig. 157.

It is made of 1-inch wrought iron piping and in sections of about four feet each, to allow of its being readily carried about from one mill to another. The couplings are long and are turned down so as to taper at either end. In the end of the rod is fastened a steel point and slots about one-fourth inch in width and fourteen inches in length are cut in each section as shown in the illustration. One side of each slot is made to project slightly beyond the side of the pipe and sharpened, as shown in the section *A-B*. In using the rod, as many sections are used as may be necessary to reach to the bottom of the bin. These are joined, the whole is thrust into the bin until it reaches the bottom, the rod is filled by turning it a few times, then withdrawn, turned upside down and the cement shaken out of it into a bag by rapping it against the side of the stock house.

A rod made with the slot running its entire length and terminating in a *T*, with two pieces of short pipe screwed into it to form a handle, is sometimes used to sample bins. The main trouble with this rod is that such a long slot weakens the sampler, and unless made of very heavy pipe it soon twists out of shape. Grain samplers may also be used to sample bins but are seldom made long enough to reach to the bottom of the bins.

Fig. 158 shows a sampler designed by Mr. Wm. P. Gano,

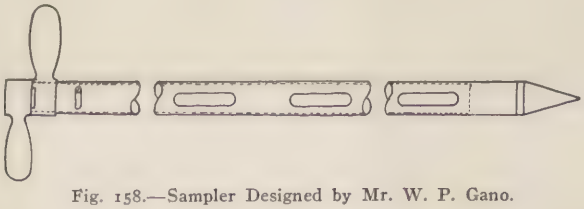


Fig. 158.—Sampler Designed by Mr. W. P. Gano.

chief chemist of the Pennsylvania Cement Company, and made by Riehlé Bros. Testing Machine Company. It consists of two brass tubes, 10 feet long, one of which fits snugly into the other. The outside tube is 1¾ inches outside diameter. Two brass handles are pinned, one to each tube, and the outside tube is provided with a bronze point. The outside tube is No. 20 brass and the

inside No. 16. Both tubes are provided with twenty-seven openings, 2½ inches long by ½ inch wide. These slots are made at corresponding points in the two tubes. One edge of each slot in the outside tube is flared outward and provided with a cutting edge. A ¼-inch brass set screw working in a slot shows when the openings are opposite. The sampler is thrust down into the cement with the inner tube turned so that the openings are closed. When the bottom of the bin is reached, the handles are turned so that the openings are opened and the tube is turned round a few times. The flared edges of the openings then scrape the cement into the tube. This sampler is one of the best for obtaining a sample from bins.

Where cement can be sampled as it goes into the bin, as is done regularly by the manufacturer, some form of automatic sampler such as described on page 496 should be installed and no mill is complete which is not so equipped.

Silo bins are usually sampled as they are filled, or after filling by drawing cement from the discharge openings. In doing the latter, a ball, or other indicator, is placed in the middle of the top of the bin and cement is drawn out at the bottom until the ball appears at the discharge. The cement drawn out is sampled at frequent intervals meanwhile.

Uniform Specifications and Methods of Testing

In order to bring about uniformity, both in the matter of inspection and of the specifications under which cement is sold, committees have been appointed by various scientific societies, chief of which have been the American Society for Testing Materials and the American Society of Civil Engineers. The latter society appointed a committee, some forty years ago, to consider methods of testing cement and received its report in 1885. Later, another committee was appointed, which reported January 21, 1903. This report was amended at various times to keep it up to date and the methods of test recommended by it are now considered the standard ones.

The American Society for Testing Materials turned its attention to the drafting of a uniform set of specifications for cement,

and its committee first reported, June 17, 1904. Since this time the report has been amended a number of times. The important amendments consisted in altering the requirements as to specific gravity and tensile strength. This set of specifications has been endorsed with subsequent revisions by The American Institute of Architects, The American Railway Engineering and Maintenance of Way Association, The Association of American Portland Cement Manufacturers, and The American Society of Civil Engineers, and later when this was formed by the Engineering Standards Committee and hence may be considered the "Standard Specification."

In the following sections under the heading *"Specification"* are given the requirements as defined by the above set of specifications while under the heading, *"Method of Operating the Test,"* is given the method of testing recommended.

Tests to be Made

The qualities which are requisite for a good Portland cement are those which insure that concrete made from it shall be of sufficient strength to withstand any and all strains, stresses and shocks to which it may be submitted, not only when first made and allowed to harden, but after the lapse of many years. The tests now applied to cement all aim to search out these qualities, or show their absence, and may be classed under two general heads, *i. e.*, those designed to show the strength of concrete made from the cement, and those designed to show its endurance. Under the first head come the tests for tensile strength, compressive strength, fineness to which the cement is ground, as this influences its sand-carrying capacity and hence its strength, and time or rate of setting, as quick-setting cement may not give sufficient time for proper manipulation of the concrete and slow-setting cement may take too long to get its strength. Under tests for endurance come the various so-called soundness tests, and possibly chemical analysis as the quantities of magnesia and of sulphur trioxide present are supposed to have an influence upon endurance.

Ordinarily cement is tested as to its:

(1) Soundness.
(2) Time of setting.
(3) Tensile strength with sand.
(4) Fineness to which it has been ground.
(5) Specific gravity.

Other tests are those of compressive and transverse strength, adhesion, resistance to abrasion, etc.

CHAPTER XX

SPECIFIC GRAVITY

Standard Specification and Method of Test

Standard Specification for Specific Gravity

The specific gravity of the cement, thoroughly dried at 100° C., shall be not less than 3.10 (3.07 for white Portland cement). Should the test of cement as received fall below this requirement a second test may be made upon an ignited sample. The specific gravity test will not be made unless specifically ordered.

Standard Method of Operating the Test

28. *Apparatus.*—The determination of specific gravity shall be made with a standardized Le Chatelier apparatus which conforms to the requirements illustrated in Fig. 159. This apparatus is standardized by the U. S. Bureau of Standards. Kerosene free from water, or benzine not lighter than 62° Baumé, shall be used in making this determination.

29. *Method.*—The flask shall be filled with either of these liquids to a point on the stem between zero and one cubic centimeter, 64 grams of cement, of the same temperature as the liquid, shall be slowly introduced, taking care that the cement does not adhere to the inside of the flask above the liquid and to free the cement from air by rolling the flask in an inclined position. After all the cement is introduced, the level of the liquid will rise to some division of the graduated neck; the difference between readings is the volume displaced by 64 grams of the cement.

The specific gravity shall then be obtained from the formula:

$$\text{Specific gravity} = \frac{\text{Weight of cement (g.)}}{\text{Displaced volume (cc.)}}.$$

30. The flask, during the operation, shall be kept immersed in water, in order to avoid variations in the temperature of the liquid in the flask, which shall not exceed 0.5° C. The results of repeated tests should agree within 0.01.

31. The determination of specific gravity shall be made on the cement as received; if it falls below 3.10, a second determination shall be made after igniting the sample as described on page 434.

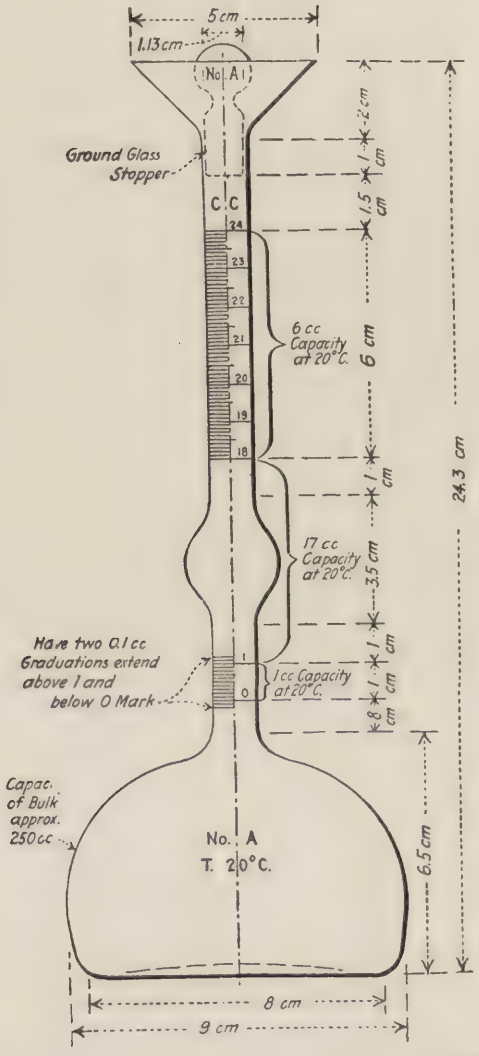


Fig. 159.—Le Chatelier's Specific Gravity Bottle, Standard Form.

Notes

A convenient method for cleaning the apparatus is as follows: The flask is inverted over a large vessel, preferably a glass jar, and shaken vertically until the liquid starts to flow freely; it is then held still in a vertical position until empty; the remaining traces of cement can be removed in a similar manner by pouring into the flask a small quantity of clean liquid and repeating the operation.

Kerosene will be found the most convenient liquid for use in taking the specific gravity of cement. It is cheap and may be easily obtained. To free it from water, place in a large bottle, together with some quicklime or a lump of calcium chloride and shake well. Allow the lime to settle, keep tightly corked and draw or pour off the oil carefully for use.

It is most important to have the temperature of the liquid the same at the time the two readings are made hence the immersion of the flask in a cylinder of water. The importance of this will be understood when it is pointed out that a change of 1° C. will effect the volume by 0.22 cc. or a specific gravity reading by 0.035. A rise in temperature will make the observed specific gravity too low and vice versa. The flask should be allowed to remain in water for at least one-half hour before the first reading is taken and fifteen minutes before the second is made, checking the temperature of the water before each reading.

The inside stem of the flask above the bulb should be wiped perfectly dry after the bulb is filled with kerosene by means of a swab of absorbent cotton on a wire, a thin roll of filter paper or a clean cloth.

A convenient method of dropping the cement in the flask is to place the weighed sample of cement on a sheet of glazed paper across the middle of which a trough has been made by folding in the palm of the hand and gradually drawing the cement into the flask in small lots by means of a flattened wire. The latter may also be used to dislodge any cement which sticks to the neck of the flask, or the flask itself may be rapped on a piece of sheet cork or blotting paper on top the table for this pur-

pose. This gentle rapping is also resorted to for the purpose of dislodging any air bubbles carried down by the cement.

The old style Le Chatelier apparatus had only one graduation below the bulb and it was necessary therefore to fill the flask to exactly this point before introducing the cement. This may be most conveniently done by means of a pipette. The writer when employing the old style bottle usually filled the bottle to a little above the graduation below the bulb, and after allowing the flask to remain in the water bath for one-half hour, the excess of kerosene was sucked off until the level reached the lower graduation on the stem by means of a piece of glass tubing drawn out to form a pipette. In order to protect the inside of the neck of the flask from wetting when withdrawing the pipette this was covered by means of a thin roll of filter paper inserted in the stem and reaching down to the bulb.

The table following will be found useful in calculating the specific gravity.

TABLE XLV.—Values of Specific Gravity in Terms of the Readings of the Le Chatelier Apparatus, when Using 64 Grams of Cement.

Cc.	0.00	0.02	0.04	0.06	0.08
19.50	3.282	3.279	3.275	3.272	3.269
0.60	3.265	3.262	3.258	3.255	3.252
0.70	3.249	3.246	3.242	3.239	3.236
0.80	3.232	3.229	3.225	3.222	3.219
0.90	3.216	3.213	3.209	3.206	3.203
20.00	3.200	3.197	3.194	3.190	3.187
0.10	3.184	3.181	3.178	3.174	3.171
0.20	3.168	3.165	3.162	3.159	3.156
0.30	3.153	3.150	3.147	3.143	3.140
0.40	3.137	3.134	3.131	3.128	3.125
0.50	3.122	3.119	3.116	3.113	3.110
0.60	3.107	3.104	3.101	3.098	3.095
0.70	3.092	3.089	3.086	3.083	3.080
0.80	3.077	3.074	3.071	3.068	3.065
0.90	3.063	3.059	3.056	3.054	3.051
21.00	3.048	3.045	3.042	3.039	3.036
0.10	3.033	3.030	3.027	3.025	3.022
0.20	3.019	3.016	3.013	3.011	3.008
0.30	3.005	3.002	3.000	2.997	2.995

TABLE XLV.—VALUES OF SPECIFIC GRAVITY IN TERMS OF THE READINGS OF THE LE CHATELIER APPARATUS, WHEN USING 64 GRAMS OF CEMENT.—(*Continued*).

Cc.	0.00	0.02	0.04	0.06	0.08
0.40	2.992	2.989	2.986	2.983	2.980
0.50	2.977	2.974	2.971	2.969	2.966
0.60	2.963	2.960	2.957	2.955	2.952
0.70	2.949	2.946	2.944	2.942	2.939
0.80	2.936	2.933	2.930	2.928	2.925
0.90	2.922	2.919	2.917	2.914	2.912

All apparatus purchased for the determination of specific gravity should be tested as to the accuracy of the graduation by sending to the U. S. Bureau of Standards for this purpose. Or the maker may be made to furnish a certificate from the bureau as to the accuracy of the apparatus. We have frequently found apparatus which gave incorrect results owing to faulty graduations. The older editions of this book give methods for checking the accuracy of the apparatus.

Other Methods

Other forms of apparatus which have been used for taking the specific gravity of cement are those of Schumann, Candlot and Jackson. These are all described in the preceding editions of this book. Their use has been superseded by the standard Le Chatelier apparatus described above.

When this apparatus is not at hand the specific gravity of cement may be determined by the use of the ordinary pycnometer or specific gravity bottle by the following method:

First weigh the bottle, empty, then fill the bottle with water and weigh. Then dry and fill with kerosene and weigh. Calculate the specific gravity of kerosene from the formula

$$x = \frac{B - p}{w - p},$$

where x = specific gravity of kerosene, B = weight of bottle full of kerosene, W = weight of bottle full of water, and p = weight of the empty bottle.

Now introduce a weighed portion of the cement into the bottle, fill with kerosene, and weigh. The specific gravity of the cement may then be found by the formula

$$X = \frac{C \times x}{B + C - D},$$

where B = weight of the bottle full of kerosene, C = weight of the cement. D = weight of the bottle and the cement and the kerosene, x = specific gravity of the kerosene as found above, and X = specific gravity of the cement. Turpentine or benzine may be used in place of kerosene.

Observations on Specific Gravity

Neither the French nor German specifications have any requirements as to specific gravity. The English specifications place the minimum limit for fresh cement at 3.15 and for cement four weeks old at 3.10.

While a minimum specific gravity clause is a feature of many specifications for Portland cement, there is probably no test of less value or which taken by itself might lead to more faulty conclusions.

Originally in the Standard Specifications for cement under the heading "General Observations," appeared the following paragraph:

"Specific Gravity is useful in detecting adulteration and underburning. The results of tests of specific gravity are not necessarily conclusive as an indication of the quality of a cement, but when in combination with the results of other tests may afford valuable indications."

Shortly after the publication of this report the writer began a series of experiments in connection with one of his assistants, Mr. L. C. Hawk, to determine the causes which tend to lower the specific gravity of Portland cement and the actual value of the test. The Committee on Technical Research of the Association of American Cement Manufacturers took up the subject and their two reports will be found in the proceedings of this association. Butler, an English chemist, also made experiments along the same line which he described in the proceedings of the Institute of Civil Engineers.

Effect of Burning on Specific Gravity

Naturally the first condition to receive attention by Meade and Hawk was the degree of burning. This was done in the following manner: A kiln was detected turning out under-burned clinker, and from this kiln twelve samples were drawn as the kiln was heated up to slightly above normal temperature. From these samples, four were selected as representing (1) very soft under-burned clinker, (2) slightly under-burned clinker, (3) normally burned clinker and (4) very hard burned clinker. These clinkers were then ground as rapidly as possible to pass a standard 100-mesh sieve and the specific gravity at once taken. The need of haste was occasioned by the fact that under-burned clinker rapidly absorbs carbon dioxide and water from the air, which lowers its specific gravity. The specific gravity of the three samples was found to be:

1. Very soft under-burned clinker 3.208
2. Slightly under-burned clinker 3.222
3. Normally burned clinker 3.214
4. Very hard burned clinker 3.234

The ground clinker was also mixed with 2 per cent plaster of Paris, and made into pats which were subjected to the steam test. At the end of two hours the pat made from the very soft under-burned clinker had entirely disintegrated. At the end of five hours the pat from the slightly under-burned clinker had become checked and partially disintegrated. The other two pats not only stood the steam test satisfactorily, but five hours longer in boiling water had no effect upon them. Thus we see that although the difference in specific gravity is only 0.026, the degree of burning in the four samples was markedly different.

The author has frequently taken the specific gravity of under-burned clinker and in no case has he ever found it below that of the standard specifications.

The experiments made by the members of the Association of American Cement Manufacturers conducted at six different mills, gave an average of 3.14 for the specific gravity of the under-burned cements and 3.18 for that of the hard burned ones.

Effect of Adulteration on the Specific Gravity

The effect of adulteration can of course be calculated accurately. The substances most available for adulteration of Portland cements in this country are natural cement, raw material or limestone and slag. Rosendale or natural cement has probably been used more than any of the others. Its specific gravity ranges between 2.8 and 3.1. In detecting a mixture of Rosendale cement and Portland cement the value of the test will depend entirely upon the specific gravity of the Rosendale. In the case of a natural cement with a specific gravity of 2.9 it would, of course, be possible to mix as much as one part Rosendale to two parts Portland, while with natural cements of higher density more Rosendale could be used.

The raw material or cement-rock of the Lehigh district has a specific gravity of about 2.7, hence very little of it could be used without lowering the specific gravity appreciably. Its dark color would also cause its presence to be suspected and chemical analysis would readily detect it. Limestones average in specific gravity about 2.8, so that only about 20 per cent of the mixture could be used without lowering the specific gravity below that called for by the standard specifications. In the case of blast furnace slag, the density of which is somewhere around 3.0 large quantities could be used without detection by the specific gravity test. The writers recently had a sample of basic slag containing 36 per cent silica, of which the specific gravity was 3.05. A mixture of one part of this slag and one part of Portland had a density of 3.12.

It would seem therefore that while the test would be of value in detecting additions of limestone or cement-rock, it is by no means an infallible one or even a reliable one for detecting admixture of Rosendale or slag.

Effect of Seasoning Cement or Clinker on Specific Gravity

It has long been known that the storage of cement causes a lowering of its specific gravity. This is easily explained by the fact that cements on exposure to air absorb carbon dioxide and

water, forming calcium carbonate and calcium hydroxide. The former has a density of 2.70 and the latter of 2.08. The effect of storage on cement is shown by the following:

TABLE XLVI.—EFFECT OF SEASONING ON SPECIFIC GRAVITY OF CEMENT.

	Specific gravity				
Sample No.	1	2	3	4	5
When made	3.19	3.21	3.16	3.15	3.20
After 28 days, undried	3.11	3.12	3.10	3.09	3.08
After 28 days, dried at 100° C.	3.16	3.18	3.14	3.12	3.14
After 6 months, undried	3.08	3.04	3.08	3.03	3.04
After 6 months, dried at 100° C.	3.13	3.09	3.12	3.09	3.09
After 6 months, ignited	3.18	3.21	3.18	3.15	3.19

Reference to the above table shows that samples 2, 4 and 5 would have failed to come up to the standard specific gravity specifications after six months, and yet, briquettes made of the samples at the same time the specific gravity determinations were made, showed the cement to be at its best, after storage for that length of time.

A sample of cement had a specific gravity of 3.21 when fresh and after lying in a warehouse three years had a specific gravity of only 3.02. Its properties at the end of that period were excellent and the only noticeable change in its condition was that it was slightly caked.

It is now generally conceded that the seasoning of cement is an advantage, and many tests by various operators show that cement gives its best strength after a storage of from three to six months. Yet it is probable that cement which has been stored this length of time will have a specific gravity of less than 3.10. If the cement does not absorb some carbon dioxide and water no benefits will be derived from seasoning, and if it does absorb them the specific gravity is bound to be lowered thereby. The absorption of 3 per cent carbon dioxide and water is sufficient to lower the specific gravity of cement below 3.10. An under-burned cement which failed when freshly made to stand a five hours' steam test without complete disintegration had

a specific gravity of 3.185. After being seasoned one month it stood five hours' steam and boiling tests perfectly, but its specific gravity had fallen to only 3.082.

Similarly it has been found that seasoned clinker made a cement of lower specific gravity than would have been the case if the clinker had been ground fresh from the kilns. Otherwise the cement is excellent. For example, a sample of clinker fresh from the coolers gave a specific gravity of 3.18; after being exposed out of doors for one month the specific gravity fell to 3.04, and after two months' exposure to 2.96. The cement made from the exposed clinker had neat strength of 677 pounds at the end of seven days and 765 pounds at the end of twenty-eight days, and a sand strength of 330 pounds in seven days and 394 pounds in twenty-eight days.

It will be seen therefore that seasoning or storage of the cement has a much greater effect upon the specific gravity than under-burning or adulteration.

Specific Gravity Upon Dried and Ignited Samples

If a sample which has been kept for some time is dried at 100° C., its specific gravity will be found to be higher than it was in the undried condition, (Refer to Table XLVI), but still not as high as when it was freshly made. If this sample is subjected to a strong ignition in a platinum crucible over a good blast lamp, its specific gravity will still further increase and may even be more than the original specific gravity of the freshly made cement.

The new specifications propose in cases where the specific gravity of cement falls below the limit prescribed by the specifications that the samples should be ignited and the specific gravity of the ignited sample taken. We have made a large number of determinations of specific gravity upon seasoned cements from which we find that practically all samples of cement when ignited give a specific gravity of between 3.15 and 3.22 and that most of them give around 3.20. This conclusion was also reached by the Committee on Technical Research of the Association of American Portland Cement Manufacturers, and by Butler.

Upon igniting a mixture of 40 per cent Rosendale and 60 per cent Portland cement having a specific gravity of 2.985 before ignition we were surprised to obtain a specific gravity of 3.20. This result was checked with practically the same result. A mixture of 40 per cent cement-rock and 60 per cent Portland cement which had a specific gravity of 2.95, gave after ignition 3.20. This would prove that the ignition of the cement and determination of the specific gravity of the ignited sample fails to give any indication of adulteration even where this has taken place to a considerable extent.

A former requirement, that cement which falls below a specific gravity of 3.10 shall also not show more than 4 per cent loss on ignition, will serve to detect additions of limestone but will not of slag or Rosendale cement, since these substances themselves show very small loss on ignition. Seasoning will also cause high loss on ignition and a well-seasoned cement or one made from seasoned clinker might easily show a loss on ignition of more than 4 per cent. If this loss on ignition is a good part of it water, the inspector may safely conclude that no adulteration has been practiced.

In conclusion it may be said that the specific gravity determination is of little value in determining whether cement has been under-burned or not. The experienced cement chemist at the mill can see at a glance by looking at the clinker if it is underburned, and the engineer or inspector can judge better by the test for soundness. It is also for the reasons given above, no indication of adulteration. If, however, the specific gravity of a cement is low, it is well to examine it a little more closely, to see if it is adulterated, by the methods outlined in Chapter XXV, on "Detection of Adulteration."

Manufacturing Conditions Affecting Specific Gravity

The above paragraphs will indicate fairly well the conditions met with in manufacturing which are likely to make a cement fail to meet the specific gravity test. The percentage of iron in the cement has a slight influence on specific gravity—the effect of a high percentage of iron being to raise the specific gravity.

Low specific gravity, except in the case of white cements, however, is not apt to be due to a low iron content in the cement. The respective percentages of the other elements seem to have little influence on the specific gravity of cement within the limits usually met with in standard Portland cement. Where the specific gravity of cement is low this is most likely to be the result of seasoning of either the cement or the clinker before grinding and the remedy in this case is obvious. Where water is sprayed on the clinker, or the latter is "seasoned" out of doors, sufficient hydration may take place to cause the resulting cement to fall below the specifications when tested as received. It ignited, however, the cement should pass the test satisfactorily.

CHAPTER XXI

FINENESS

Standard Specification and Method of Test

Specification.—The residue on a standard No. 200 sieve shall not exceed 22 per cent by weight.

32. *Apparatus. Method of Operating the Test.*—Wire cloth for standard sieves for cement shall be woven (not twilled) from brass, bronze, or other suitable wire, and mounted without distortion on frames not less than 1½ inches below the top of the frame. The sieve frames shall be circular, approximately 8 inches in diameter, and may be provided with a pan and cover.

33. A standard No. 200 sieve is one having nominally an 0.0029-inch opening and 200 wires per inch standardized by the U. S. Bureau of Standards, and conforming to the following requirements:

The No. 200 sieve should have 200 wires per inch, and the number of wires in any whole inch shall not be outside the limits of 192 to 208. No opening between adjacent parallel wires shall be more than 0.0050 inch in width. The diameter of the wire should be 0.0021 inch and the average diameter shall not be outside the limits 0.0019 to 0.0023 inch. The value of the sieve as determined by sieving tests made in conformity with the standard specifications for these tests on a standardized cement which gives a residue of 25 to 20 per cent on the No. 200 sieve, or on other similarly graded material, shall not show a variation of more than 1.5 per cent above or below the standards maintained at the Bureau of Standards.

34. *Method.*—The test shall be made with 50 grams of cement. The sieve shall be thoroughly clean and dry. The cement shall be placed on the No. 200 sieve, with pan and cover attached, if desired. The sieve shall be held in one hand in a slightly inclined position so that the sample will be well distributed over the sieve, at the same time gently striking the side about one hundred and fifty times per minute against the palm of the other hand on the up stroke. The sieve shall be turned every twenty-five strokes

about one-sixth of a revolution in the same direction. The operation shall continue until not more than 0.05 gram passes through in one minute of continuous sieving. The fineness shall be determined from the weight of the residue on the sieve expressed as a percentage of the weight of the original sample.

35. Mechanical sieving devices may be used, but the cement shall not be rejected if it meets the fineness requirement when tested by the hand method described in Section 34.

Notes

Foreign Specifications for Fineness

The English, German and French specifications all call for fineness tests to be made on sieves having 900 to 4,900 meshes per square centimeter respectively. The former is equivalent to 76 meshes to the linear inch and the latter to 180 meshes to the linear inch. The diameter of the wire used in the former is 0.002 inch and in the latter 0.0044 inch. This makes the openings in the English 180-mesh sieve 0.0036 inch square while in the U. S. Standard 200-mesh sieve they are 0.0029 inch square. The requirements of the three foreign specifications referred to are as follows:

	Highest residue on sieve	
	900-mesh	4900-mesh
	%	%
England	3	18
France	10	30
Germany	5	–

All of the above three specifications call for the test to be made on 100 grams.

Errors in Sieves

In purchasing sieves for making the fineness test, care must be exercised to see that they are within the limits prescribed by the standard rules, for there are many so-called standard sieves on the market which are anything but standard. I have seen a No. 100 test sieve bearing the name of a well-known firm, which

makes a specialty of supplying apparatus for cement testing, that was made of wire cloth containing, to the linear inch, 90 meshes one way by 93 the other. Not only may standard sieves not contain the proper number of meshes but the wire from which the cloth is woven may be larger or smaller than the size called for in the standard method. This will reduce or increase, as the case may be, the size of the openings of the sieve. Not only may the sieves vary from the standard by reason of incorrect mesh, but also by reason of irregular spacing. That is, the wires may be nearer together in some places than in others, leaving large openings at the latter points for the cement to drop through.

On purchasing sieves they should be examined as to the regularity of the spacing by holding them to the light and also the number of meshes to the inch should be counted. For this latter purpose, small magnifying glasses such as are used for testing linen are convenient. These consist of a small lens, mounted on

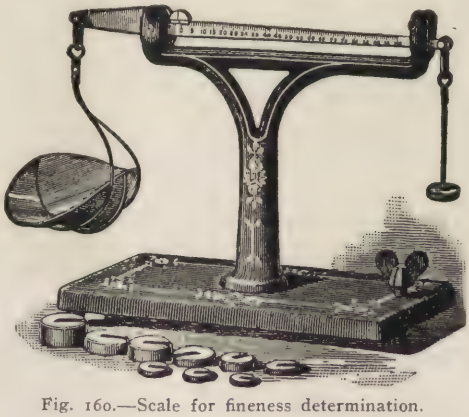


Fig. 160.—Scale for fineness determination.

a stand, in the base of which is an opening exactly one-half inch square. The opening is placed over various parts of the sieve and the number of meshes counted. Where such an instrument is not at hand, an opening of this size may be cut in a piece of cardboard and the meshes counted by the aid of a small reading or pocket magnifying glass. Sieves may also be calibrated by com-

paring them with other sieves of known value. Or a sample of standard ground quartz may be kept for this purpose. Any holes or irregularities in test sieves should be stopped up with solder.

A convenient balance for use in making sieve tests is shown in Fig. 160. The beam is graduated into 1/1000 of a pound, hence if one-tenth pound (= about 45 grams) is taken for the test each of the small divisions on the beam will represent 0.1 per cent residue.

Other Methods

Methods of Sieving, Sieves, Etc.

Where many sievings have to be made every day, the use of a sieve without top and bottom is the general plan. In this case the sieving is done over a large piece of paper or oilcloth. When it is desired to ascertain if the operation has been completed, the material on the paper is rolled to one side by lifting the edge of the paper, thus exposing a clean surface over which the sifting may be continued and the amount passing through the sieve observed. An experienced operator will be able to tell, by his eye and sense of time, when the operation is finished, without recourse to balance and weights. In place of striking the sieve against the palm of the hand some operators bounce one side of it, gently up and down, on a small block of wood, taking care not to bounce any of the material over the top of the sieve. The use of shot also greatly hastens the operation of sieving, as the bouncing of these latter, on the wire cloth of the screen, keeps the meshes of the latter open. To separate the shot from the coarse material preparatory to weighing the latter, pass the mixture through a 10- or 20-mesh screen.

When tests are made by using sieves without a top the sides of these should be high in order to avoid bouncing the material out of the apparatus. If the sieving is done by bouncing the sieve up and down on a block the sides of the sieve should be at least six inches high.

It is important that the sieve be rotated as indicated during sieving. Griesenauer found that the results of the test are materially affected by the position of the warp and the shoot wires with reference to the motion of the sample across the wires. With the same standard sieve he found a difference of 1.38 per cent between the tests made with the sieve in the two positions.

Various forms of mechanical shakers for doing away with the manual labor incident to hand sieving have been devised and are quite generally used in spite of the fact that the hand method is specified by the standard methods of testing.

One of the best forms of mechanical shaking sieves is that shown in Fig. 161. This apparatus is manufactured by the W. S. Tyler Company, Cleveland, O., and is known as the "Ro-tap Testing Sieve Shaker." This machine operates as its

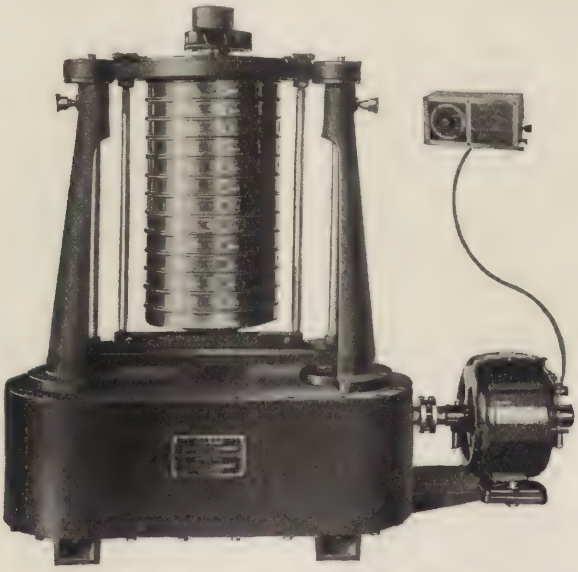


Fig. 161.—Tyler Ro-tap testing sieve shaker.

name indicates so as to give the sieve the same circular and tapping motion given testing sieves in hand sieving. The results are comparable with careful hand sieving and are better than can be obtained with any but the most conscientious operators. A

sieve test with this machine requires 20 minutes. The machine will hold six sieves of regulation height or three sieves with pan attached making it passible to test three samples at once, or one sample through six different size sieves.

Determining the Flour in Cement

A number of devices have been proposed for determining the flour in cement. The chief difficulty with them all seems to be standardization. Each one will give a different result from the other, as we would suppose, for there is no specification as to what is meant by flour, and each apparatus takes out a size different from the other.

Practically all of these forms of apparatus depend upon the suspension of the finer particles of the cement in air, benzene, kerosene, water, etc. A number of them were described in *The Engineering Record* of August 20, 1904, page 234. As we have said, the difficulty with all of them is that each would report a different percentage of the cement as flour. Even if they were so calibrated as to give concordant results, these figures would mean nothing more than the sieve test carried a little further. We do not know how fine cement has to be ground in order to "carry sand," although we know that it must be ground considerably finer than merely sufficient for it to just pass the 200-mesh sieve. For experimental purposes it is highly important to obtain some form of apparatus which will enable the finer particles of the cement to be sorted out and graded, in order that the point of fineness at which the sand carrying capacity begins to approach that of ordinary commercial cements may be determined. 'Such an apparatus, after this point has been determined, would have a practical value, because of two cements the one having the greatest percentage of such "active" particles would be the best ground.

The Germans now employ a sieve having 250 meshes to the inch as a standard in place of the No. 200 American standard. Messrs. J. Gantois et Cie of St. Die, France (Ebstein Bros., 60 Grant St., New York) advertise a 300-mesh sieve. Both of these sieves will be found of use in studying the fineness of

cement. Neither of them however is fine enough to pass only active material and reject all coarse or inactive particles and for this latter recourse must be had to one of the suspension methods given below. Something may be gained by determining the fineness on the No. 100, No. 200 and No. 250 sieves and plotting the results into a curve of which one set of ordinates represents the percentage of material passing and the other the area of the openings of the screens.

Suspension Method

The form of apparatus devised by the author for determining the flour in cement by suspension in a liquid is modeled after

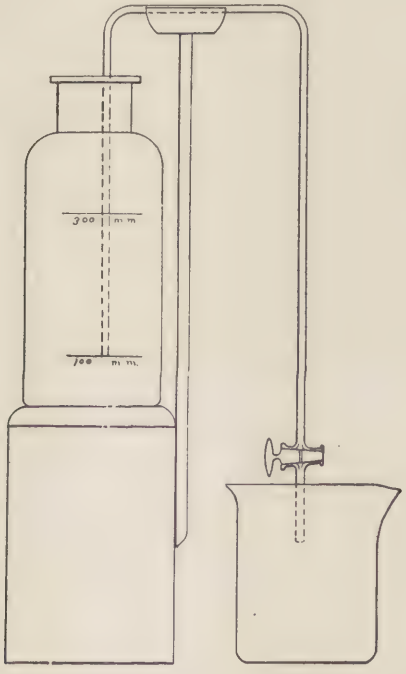


Fig. 162.—Apparatus for determining flour in cement by suspension in liquid.

the silt cylinders used for soil analysis. Fig. 162 shows the apparatus. It consists of a cylinder of at least 300 millimeters height and not too great diameter provided with a cork or stopper for closing it and a siphon for drawing off the liquid and suspended matter. The lower end of the siphon is closed by a rubber tube and pinch-cock and the upper one is bent as shown. Strips of paper or file marks are made on the cylinder, one near the top and the other exactly 200 millimeters below this one. In use, 100 grams of cement are introduced into the cylinder and the latter filled with kerosene freed from water (as described on page 555 under specific gravity) to the upper mark and shaken well. It is then placed on a block, the siphon, which should be full of kerosene inserted until its opening is level with the lower mark, and exactly ten seconds after the cylinder was placed on the block the pinch-cock is to be opened and the liquid siphoned off to the lower mark. This process is repeated until the liquid above the lower mark settles practically clear in ten seconds. The residue in the cylinder, or else the suspended matter, is then collected on a filter and its weight determined. From this the percentage of flour is calculated and reported as "particles having a settling value in kerosene of less than 20 millimeters per second." These can be again divided into two portions, by allowing fifteen seconds to settle, when the value will be $200 \div 15$ or $13\frac{1}{3}$ millimeters per second, etc.

If desired, the size of the largest of these particles can then be measured under the microscope.

The Griffin-Goreham Flourometer

The Griffin-Goreham standard flourometer is shown in Fig. 163 and is used to some extent in England. The Braun Apparatus Company, Los Angeles, Cal., are the American importers. This apparatus consists of two parts. An aerometer or blower and the apparatus proper or flourometer. The blower consists of the customary bell and water tank and is merely used to furnish a constant supply of air to the apparatus. The flourometer itself (Fig. 164) consists of a long brass tube, *T* resting upon a stand.

The separation of the coarse and fine particles takes place in this. The tube is surmounted by a double walled dome, *W*, covered with a top, *O*. The walls of this dome are perforated

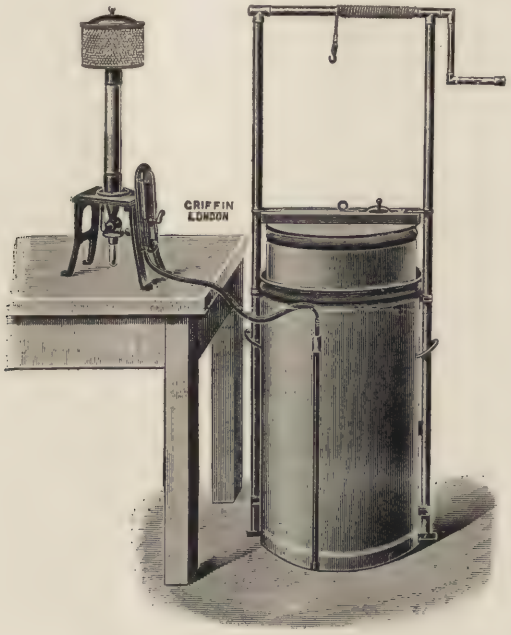


Fig. 163.—Griffin-Goreham flourometer.

and the spaces in between them (*W*) are filled with cotton. This serves to catch all the dust and prevents this being blown into the laboratory. The lower part of the brass tube, *T*, terminates in a cone-shaped brass casting, *F*, which rests upon the stand. A three-way stop-cock provided with a pointer to show the direction of the opening, is placed at the lower end of the cone and beneath this a glass tube *R*, which serves to catch the coarse particles.

The sample of cement should be dried for an hour at 110°. The pointer of the stop-cock should be at right angles to the brass tube *T*. The tube *T* is removed and about one gram of the cement is then introduced into the funnel *F*. The bell of the

aerometer is now raised to its full extent and the air pressure noted.

The pointer of the stop-cock is next turned parallel with the tube and the air allowed to blow through the apparatus for ten minutes. At the end of this time the air pressure is turned off, when the coarse particles from which the cement has been sepa-

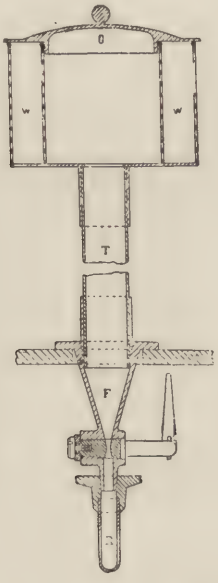


Fig. 164.—Details of the Griffin-Goreham flourometer.

rated drop into the receptacle *R*. This residue is weighed and the difference is of course flour.

Any blower which will furnish air at a steady and standard pressure may be used in place of the aerometer described. Two large cans set at constant vertical distances apart, such as one on the table and one on the floor, for instance, will serve, the upper one being filled with water which flows into the lower, forcing out the air in the latter. The objection to all these water blowers is of course the fact that the air is more or less

damp. Best results will be obtained by passing the air through a rather large drying tower filled with calcium chloride or better still pumice stone drenched with strong sulphuric acid.

The Pierson Air Analyser

This apparatus has been considerably improved by the U. S. Bureau of Standards.

Figure 165 represents the Bureau of Standards old type air analyser.[1] According to correspondence between the author and the head, the Bureau is developing a new type of apparatus but is not as this book goes to press ready to give out information as to this.

Referring to Fig. 165, *1* is a reostat in series with the motor armiture affording speed control, *2* is a ⅛ horsepower motor, *3* is a blower with a rated capacity of 12 cu. ft. per minute at 4 lbs. pressure, *4* is a grease trap, *5* is an automatic pressure regulator, *6* is a mercury gauge for indicating the pressure of the air delivered to the analysis. *7* is a detachable glass bulb provided with a set of three interchangeable nozzles which afford separation of the cement into portions corresponding to 350, 500 and 1000 mesh sieves respectively. *8* separating stack, *9* supporting tripod, *10* electric tapper to minimize adherence of dust to separating stack, *11* dust collector consisting of a flannel sack which when the apparatus is in use is drawn up over the frame.

The sieve relations are based on two dimensional microscopic measurements of cement particles. The relative sizes of the separation of the standard No. 200 sieve and the air analyses by this system of measurements are as follows:

No. 200 sieve	0.11 mm.
No. 350 sieve (air analyses)	0.06 mm.
No. 500 sieve	0.04 mm.
No. 1000 sieve	0.02 mm.

This method of designating the air analyser separations in terms of sieve mesh is for comparative purposes only as such fine sieves cannot be constructed.

I have found such apparatus in general more satisfactory than the Gary-Lindner apparatus described below. On the other hand

[1] U. S. Patent No. 1,186,525 to J. G. Pearson. Also Bureau of Standards Technologic Paper No. 48.

the Gary-Lindner apparatus is of course suitable for collecting a quantity of flour of various degrees of fineness and testing this

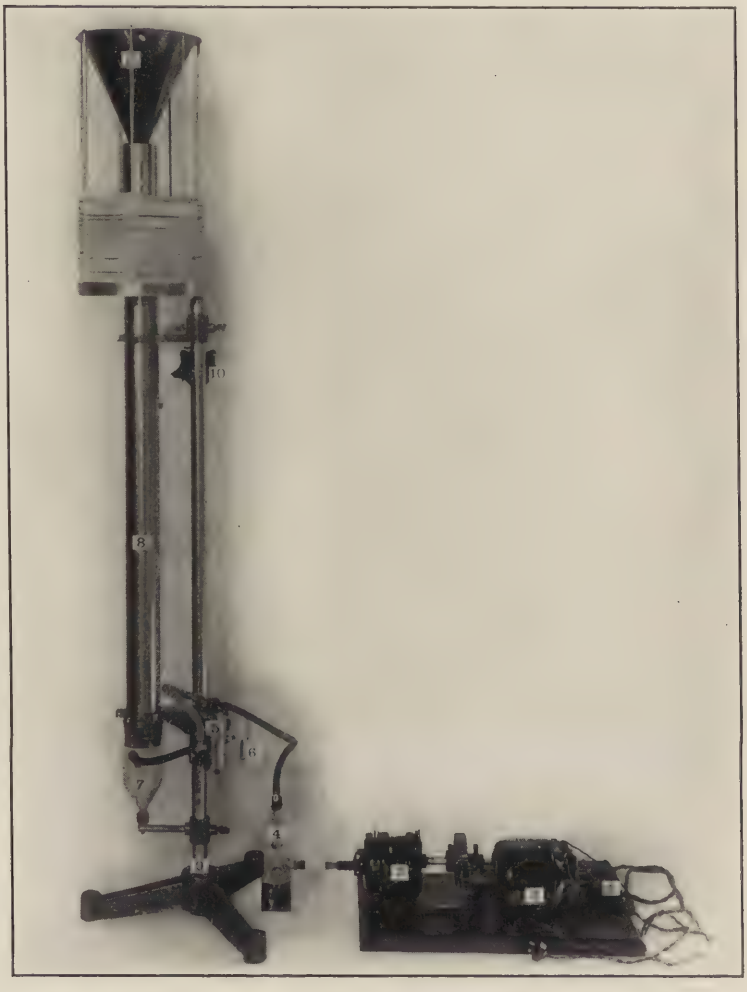


Fig. 165.—The Pearson Air Analyses of the U. S. Bureau of Standards.

with sand for strength. At the present time no very satisfactory apparatus is at hand and no one of the three methods given

can be said to give entirely satisfactory results. Some idea, however, can be formed as to the relative amount of flour by studying various cements under exactly the same conditions, and the writer has employed them to advantage in studying the various types of grinding machinery with reference to the relative amount of flour produced by these latter.

The Gary-Lindner Apparatus

The apparatus (Fig. 166) consists of three glass tubes, *a*, the lower ends of which are united by pieces of large rubber tubing to three glass funnels into which small glass tubes have been melted. Through these small tubes air is supplied. The cement

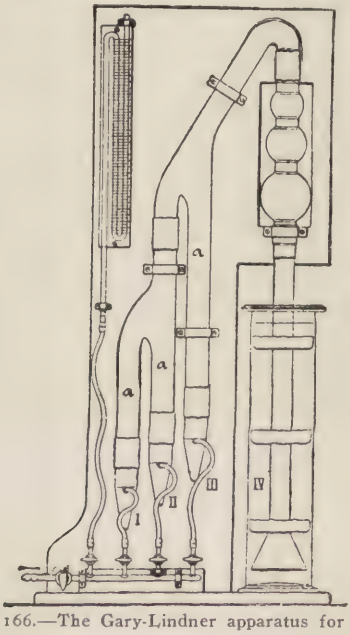


Fig. 166.—The Gary-Lindner apparatus for flour.

must be first dried perfectly. Twenty grams of the cement to be tested are placed in the funnel I, then air is blown in at a pressure of 100 millimeter water column. The glass cocks permit the adjustment of the air supply to each funnel; the pressure is noted

on the U-manometer. The funnels I, II, III will enter into operation one after the other and at the end there will remain a quantity of powder in each of the funnels. The finest flour will pass out of the glass tube III and will be arrested in the glass receptacle, IV. If the air pressure is produced by a hydraulic blower, the air must be dried before entering the funnels, as described above.

Observations on Fineness

Effect of Fineness on the Properties of Portland Cement

The effect of the fineness to which Portland cement clinker is ground upon the physical properties of the resulting cement is well understood as the following quotation from the Progress Report of the American Society of Civil Engineers will show:

"18. *Significance.* It is generally accepted that the coarser particles in cement are practically inert, and it is only the extremely fine powder that possesses adhesive or cementing qualities. The more finely cement is pulverized, all other conditions being the same, the more sand it will carry and produce a mortar of a given strength."

The two properties of cement most affected by the fineness of the product are the setting time and the sand carrying capacity. All the properties of the cement are of course influenced to some degree.

Influence on Color

The color of clinker itself is practically black. As the clinker is ground the color becomes lighter, until at a fineness of 75 per cent passing the No. 200 test sieve, the color of the commercial product, a light buff, is reached. Cement ground so fine that 95 or 100 per cent of it will pass the No. 200 test sieve is of a somewhat lighter shade than cement ground to the ordinary fineness of 75 per cent passing this sieve. At the same time, no manufacturer would care to go to the increased expense of grinding the cement to such an extreme degree of fineness merely for the sake of a slightly lighter color, nor would even

sidewalk and concrete block men care to pay the increased cost of such cement simply to obtain cement of a slightly lighter shade.

Influence on Soundness

Fine grinding will to some extent help the soundness of the cement. This is shown by Table XLVII.

This gives four instances in which soundness was helped by fine grinding, but in order to obtain four instances many samples of unsound cement were ground, and the majority of them failed to become sound even after being ground to an impalpable powder. Fine grinding and seasoning, however, usually produced the desired results. That is, an unground cement after seasoning, say one week, failed to pass the boiling test, but the same cement ground so fine that none of it remained on the No. 200 test sieve passed the test after seasoning one week. The grinding no doubt here breaks up the small pieces of clinker and allows the air to slake out the injurious component. In this connection, it may be said, that if the coarse particles, *i. e.*, those remaining on the No. 200 sieve, are separated from the cement and ground to a fineness of 75 per cent through the No. 200 sieve, the resulting product is usually unsound. It is also usually quick-setting, due to the fact that the sulphate nearly all passes into the fine powder. If 1 per cent of plaster of Paris is added to the powder, its setting time is normal but it is still unsound. If the powder is then seasoned for a few days it becomes sound.

TABLE XLVII.—Showing Effect of Fine Grinding of Cement on Soundness.

	Result of five hour steam test (A. S. C. E.)		
	As received	Ground to pass No. 200 sieve	Ground to an impalpable powder
1	Checked	Sound	.....
2	Checked	Sound	.....
3	Checked	Slightly checked	Sound
4	Checked	Slightly checked	Sound

It would, however, be a waste of energy for the manufacturer to make a sound cement by grinding one unsound at ordinary fineness to say 100 per cent passing a No. 200 test sieve, as by grinding the much softer raw materials to a fineness of only 95 to 98 per cent through the 100-mesh sieve he would be practically sure of obtaining the same results, provided the composition of the mixture and the burning of the clinker were satisfactory. At the same time, if the manufacturer found it advantageous to grind his cement to a fineness of 90 to 95 per cent through a No. 200 test sieve, he would find that it has some beneficial effect upon the soundness also, and that this effect was most marked where the cement had a chance to season or age as it usually does.

Influence on Setting Time

The influence of fineness upon the rate of set of cement is in some instances quite marked; in other instances this is much less noticeable. If any effect is produced at all, and there generally it, it is to make the cement quicker setting,—in some instances, so quick-setting as to be unfit for use: and often, where this is the case, additions of plaster of Paris fail to retard the set sufficiently to allow the cement to be used. In Table XLVIII are given a number of instances illustrating the influence of fine grinding upon setting time.

TABLE XXIX.—Influence of Fine Grinding of Cement Upon Its Setting Time.

	Per cent passing a No. 200 sieve.					
	75	80	85	90	95	100
Cement number	Setting time (initial set) in minutes					
1	255	246	192	75	12	2
2	105	106	100	100	22	6
3	120	115	100	95	60	35
4	240	200	180	115	60	30
5	240	210	110	55	15	5
6	200	190	175	100	25	2
7	100	100	90	80	25	5
8	115	105	100	75	30	10

The question of the influence of fine grinding upon the set is an important one, for upon this will depend to a large degree

the ability to grind cement to the point where all of it is rendered useful, and where it contains no inert matter except that present chemically and not due to coarseness. The composition of the cement unquestionably has something to do with the effect of fine grinding. High-alumina and low-lime cements seem to have their setting time most affected by finer grinding. High lime, soft-burned and low-alumina cements do not seem to be so much affected.

Cements low in lime are often quick-setting, and if a sample of cement is sieved through a No. 200 test sieve and analyses are made of both the coarse residue and the fine portion passing, the former will in most cases be found lower in lime than the latter. It is natural that the softer portions of the clinker should constitute the greater part of the impalpable powder in ordinary Portland cement. When the cement is ground still finer the harder portions are broken up, and these harder portions are probably responsible for the "quick set" of finely ground cement, owing to the fact that they are lower in lime and are burned to a high degree of vitrification. It is certainly possible, even probable, that if it is found advantageous to grind cement to a much greater degree of fineness than is now practiced, it will also be found necessary to grind the raw material to a higher degree of fineness, in order to allow the making of very highly basic cement, in which the highest possible amount of lime is obtained. If it is desirable to get rid of all the physically inert material by fine grinding of the clinker, it is also equally desirable to have in the cement all of the chemically active element possible.

I am strongly inclined to believe that it will be possible to grind cement very fine without influencing the set unfavorably, by properly adjusting the composition of the clinker and the degree of burning. If the finer particles of cement, not merely the particles which pass a No. 200 sieve but the impalpable dust, are separated from the cement, it will usually be found that this very fine material sets normally, showing that it is possible to grind some part of the cement at least to an impalpable powder. It is also now generally agreed that it is this fine powder which is the active constituent in cement. Hence it follows that the

active portion of cement is not quick-setting even when finely ground, and that there is some undesirable element in the coarser and at present inert particles of the cement which is liberated or rendered active by the grinding. The problem will therefore undoubtedly be to keep out the undesirable element from the clinker and to increase the desirable one. I have no doubt that by the time grinding machinery has been perfected which will reduce cement to the fineness of 100 per cent through a No. 200 test sieve on a commercial basis, the chemical side of the question will have been solved. Indeed, experiments which I have made indicate a solution of the problem. Under present conditions it would be practically impossible to produce commercially a cement much finer than 90 per cent passing a No. 200 sieve, if indeed it would be possible to reach even this fineness, and at this nothing more than a slight shortening of the setting time of properly proportioned cements should be met with.

The Structural Materials Laboratory, Chicago, found[1] that the normal consistency of cement is increased with the fineness of grinding and that about 0.1 per cent of water (in terms of the weight of cement) must be added for each 1 per cent reduction in residue on the No. 200 sieve.

Effect of Fineness upon Strength

A number of experiments made by the author to determine the effect of finer grinding upon the tensile strength of Portland cement proved the following general facts.

1. That the neat strength is lowered by finer grinding.
2. That the sand strength is increased by finer grinding.

Table XLIX gives the results obtained in one of the most carefully made of these tests.

Referring to Table XLIX we see that the neat strength is decreased by fine grinding. This decrease is as follows: Grinding to 85 per cent fine decreases the seven-day neat tensile strength 17 per cent from the figures of the 80 per cent fine. Grinding to 90 per cent fine decreases the strength 21 and 20 per cent respectively for the same periods. Grinding to 95 per

[1] *Bul. No. 4,* Structural Materials Laboratory.

TABLE XLIX.—Strength of the Same Cement Ground to Various Degrees of Fineness.

Age in days	Neat or sand	Per cent passing a No. 100 sieve				
		93.9	95.8	97.4	99.0	100.0
		Per cent passing a No. 200 sieve				
		80	85	90	95	100
		Tensile strength in lbs. per sq. in.				
1	Neat	369	241	308	282	200
7	Neat	955	796	749	627	558
28	Neat	963	849	775	626	594
7	1 : 3 sand	235	284	351	363	382
28	1 : 3 sand	297	353	468	498	576
7	1 : 4 sand	160	204	234	247	263
28	1 : 4 sand	224	266	324	377	392

Note:—Each value is based on five briquettes. Each portion is from same lot of cement. One operator made all tests.

cent fine decreases the strength 34 and 35 per cent and grinding to 100 per cent fine decreases it 42 and 38 per cent. In general it will be seen that the decrease in neat strength due to fine grinding is about the same for both the seven-day and the twenty-eight-day periods.

Referring to the sand tests it will be seen at a glance that the increase in sand strength due to finer grinding is large. Increasing the fineness from 80 to 85 per cent, increases the seven-day 1 :3 sand strength 21 per cent; further grinding to 90 per cent increases it to 45 per cent; grinding to 95 per cent increases it to 54 per cent, while grinding to 100 per cent increases it to 63 per cent over the 80 per cent strength. The 1 :4 sand strength is increased by practically the same percentage. The increase upon the twenty-eight-day sand tests due to finer grinding is even larger.

In this series of tests the original cement gained but little neat strength between these two periods. Fine grinding will decrease not only the neat strength but also the percentage of gain between

these two periods as well. An example of this is given below. In this experiment a lot of cement, just as received from the

TABLE L.—Showing Effect of Finer Grinding on Long-Time Tests of Cement.

Tensile Strength in Pounds per Square Inch.

	Neat						
	1 day	7 days	28 days	3 mos.	6 mos.	1 year	2 years
As received	327	630	725	720	760	825	850
Ground to pass a No. 200 sieve	210	525	540	540	560	575	560
	1 : 3 mortar						
	1 day	7 days	28 days	3 mos.	6 mos.	1 year	2 years
As received	...	278	357	387	390	410	425
Ground to pass a No. 200 sieve	...	480	555	575	615	623	640

mills, was divided into two parts, one of which was tested just as it was and the other was ground to completely pass a No. 200 sieve, and then tested. Table L gives the results obtained on the two samples.

Limitations of the Sieve Test

The fineness to which cement is ground is an important point. Since cement is always used with sand, the strength of the mortar increases with the fineness of the cement, because the greater is the covering power of the cement, *i. e.*, the more parts of cement come into action with the sand. A test for fineness is nearly always included in cement specifications, as the indications from a fair degree of fineness coupled with proper tensile strength are that the cement will give good results when used with sand.

At the same time the most rigid fineness specification could be filled by a cement which would be many degrees too coarse. Some of the older specifications could be easily filled by a product which would show almost no setting qualities and no sand-carrying capacity. If a sample of clinker is crushed in an iron mortar by a pestle and sieved as fast as it is ground through a 100-mesh

screen, a product will be obtained 100 per cent of which will pass a 100-mesh screen. Many of the older specifications call for only 90 per cent. If a pat is made of this cement it will just about cohere. If, however, the fine particles are sieved through a 200-mesh screen and the flour washed off the coarse particles by benzine and the latter driven off by heat, the product will still all pass a 100-mesh sieve, and yet will have no setting properties. If another sample is ground in a mortar and sieved after every few strokes of the pestle through a 200-mesh screen, it will all pass a 200-mesh sieve and yet will nevertheless be almost worthless as a cement. When washed free from its flour with benzine it will just about hold together. In the writer's laboratory there was a Braun's gyratory muller for grinding samples, in which the grinding is done by an enclosed round pestle revolving in a semi-hemispherical mortar. In the bottom of the mortar is a hole which can be stopped by a plug. The grinding may be done in two ways, one by feeding the sample into the hopper in the cover and allowing it to work its way out at the bottom, then sieving out the fine material from the coarse, and returning the latter through the grinder, and so on until all has passed the sieve. The other, by placing the plug in the bottom of the mortar and allowing the pestle to work upon the material until the latter has reached the desired fineness. Two samples of cement were prepared from the same lot of clinker by these methods. One sample, the one made by passing the clinker through the muller and sieving out the 200-mesh particles after each grind, would, of course, all pass a 200-mesh sieve. The other sample, the one made by grinding the whole sample to the desired fineness without screening, tested 96 per cent through a 100-mesh sieve and 76.5 per cent through a 200-mesh sieve. Sand briquettes were made of these two lots of cement with the following results.

	7 days pounds	28 days pounds	3 months pounds	6 months pounds
Samples made by grinding and screening to fineness (all 200-mesh)	Broke in clips	Broke in Clips	Broke in Clips	28
Grinding to fineness without screening	215	295	324	318

The cementing value of Portland cement depends upon the percentage of those infinitesimal particles which we call flour. No sieve is fine enough to tell the quantity of these present. At the same mill it is probable that the sieve test is relative but to the engineer who is called upon to examine the product of many mills using different systems of grinding the sieve test, is hardly to be expected to give the relative percentage of flour in each. The product of the Griffin mill and of the ball and tube mill probably differ much in the percentage of flour present, even when testing the same degree of fineness on the 200-mesh sieve. Even with the ball and tube mill system one ball mill and two tube mills would probably give a product with a higher percentage of flour than one tube mill and two ball mills, even when the cement was ground to the same sieve test. The size screen on the ball mills probably also influences the percentage of flour in a product of a certain fineness.

Effect of Fineness of the Cement on the Resulting Concrete

The Structural Materials Laboratory, Chicago, has made a careful study of the effect of the fineness of cement on the properties of concrete:[1] Their conclusions follow.

In general, the strength of concrete increases with the fineness of a given lot of cement, for all mixes, consistencies, gradings of the aggregate, and ages of concrete. The cements with residues lower than about 10 per cent were inclined to give erratic results in the strength tests; one lot showed an abnormal increase, and two a pronounced decrease in strength as compared with the other tests on coarser cements in the same lot.

For residues higher than 10 per cent the strength of concrete varies approximately inversely as the residue on the No. 200 sieve.

Fine grinding of cement is more effective in increasing the strength of lean mixtures than rich ones.

Fine grinding of cement is more effective in increasing the strength of concrete at seven days than at ages of twenty-eight days to one year.

[1] *Bull. No. 4,* Structural Materials Laboratory. D. A. Abrams, Lewis Inst.

For the usual range of consistencies the effect of fineness of cement is independent of the consistency of the concrete. The rate of increase in strength with fineness is lowered for very wet mixtures.

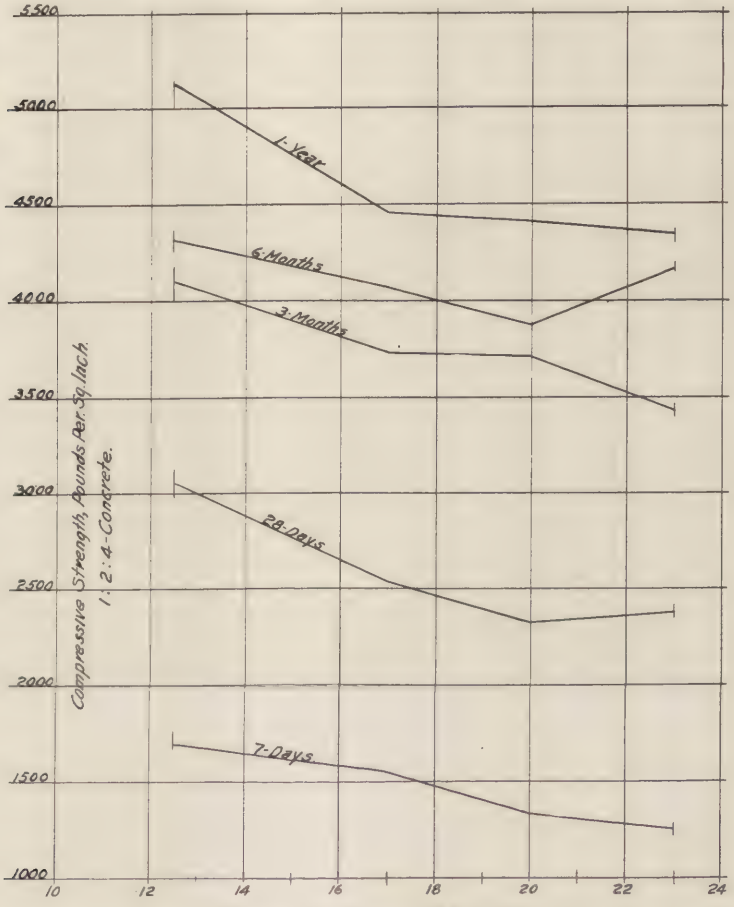


Fig. 167.—Effect of fineness of cement on concrete (From Prof. Abrams' test A-1).

Ordinary concrete mixtures at twenty-eight days show an increase in strength of about 2 per cent for each 1 per cent re-

duction in the residue of the cement on the No. 200 sieve. At seven days, three months and one year the corresponding increases in strength are about 2.5, 1.7 and 1.4 per cent.

The decreased benefit of fine grinding of cement with the age of the concrete does not bear out accepted opinion that the coarser particles of cement do not hydrate, but indicates that the principal result of finer grinding is to hasten the early hardening of the concrete.

For the richer mixtures and the consistency necessary for building construction, the fineness of the cement has no appreciable effect on the workability of concrete as determined by the "slump" test. For leaner mixtures and wetter consistencies the finer cements showed a somewhat greater "slump" than the coarser cements.

The unit weight of cement decreases with fineness. For the cements used in these tests the weight varied from 76 (residue of 2.4 per cent) to 108 pounds per cubic foot (residue 43.3 per cent). For the usual range in fineness the weight is lowered about three-fourth pound per cubic foot for each 1 per cent reduction in the residue on the No. 200 sieve.

Fig. 167 shows graphically the influence of finer grinding of cement on the strength of concrete and is taken from the above-mentioned bulletin.

Effect of Manufacturing Conditions on Fineness

Theoretically provided the cement mill is equipped with the proper grinding machinery it is within reasonable limits entirely a matter of choice with the manufacturer how fine the cement is to be ground. As the grinding of the clinker is one of the most expensive operations in the manufacture of cement, however, this choice is generally influenced by considerations of economy. Poor equipment often makes the grinding of cement expensive and limits the manufacturer to a fineness approximating too closely the lower limits of the specifications for the comfort of the chemist who is responsible for the quality of the product. In the chapters of this book devoted to "Grinding Machinery" and "Grinding the Clinker," the mechanical aspects of

the problem are fully dealt with and to these the reader is referred for a discussion of the proper machinery, etc., to be employed in grinding clinker.

The chemical composition of the clinker itself has an important bearing on the facility with which it can be ground. A high percentage of iron in the clinker will make the latter very hard to grind and will increase materially the repairs on the mills used for grinding. It is quite probable that other things being equal the facility with which clinker can be ground increases as the iron oxide content decreases.

On the other hand, clinker high in lime (or with a high lime ratio) is easier to grind than one low in lime. Attention to this has been called in the chapter on "Grinding the Clinker" and the matter discussed quite fully then. High silica cements are easier to grind than those high in alumina. This may be due, however, to the greater likelihood that the latter are burned to a higher degree of vitrifaction.

The degree of burning of course influences the facility with which clinker can be ground, the harder burned material being naturally the more difficult to pulverize. The statement is also made that the clinker of the wet process is more easily ground than that from the dry. Hot clinker is harder to grind than that which is perfectly cold, as is also damp or wet clinker. Clinker which has been seasoned out of doors, or where moisture can reach it, is more easily ground than fresh clinker, provided it is not damp when fed to the grinding mills.

CHAPTER XXII

TIME OF SETTING

Standard Specification and Method of Test

6. *Specifications.*—The cement shall not develop initial set in less than forty-five minutes when the Vicat needle is used or sixty minutes when the Gillmore needle is used. Final set shall be attained within ten hours.

Normal Consistency

36. *Mixing Cement Pastes and Mortars.*—The quality of dry material to be mixed at one time shall not exceed 1,000 grams nor be less than 500 grams. The proportions of cement, or cement and sand, shall be stated by weight in grams of the dry materials; the quantity of water shall be expressed in cubic centimeters (1 cc. of water = 1 gram). The dry materials shall be weighed, placed upon a non-absorbent surface, thoroughly mixed dry if sand is used, and a crater formed in the center, into which the proper percentage of clean water shall be poured; the material on the outer edge shall be turned into the crater by the aid of a trowel. After an interval of one-half minute for the absorption of the water the operation shall be completed by continuous, vigorous mixing, squeezing and kneading with the hands for at least one minute.[1] During the operation of mixing, the hands should be protected by rubber gloves.

37. The temperature of the room and the mixing water shall be maintained as nearly as practicable at 21° C. (70° F.).

38. *Apparatus.*—The Vicat apparatus consists of a frame *A* (Fig. 168) bearing a movable rod *B*, weighing 300 grams, one end *C* being 1 centimeter in diameter for a distance of 6 centimeters, the other having a removable needle *D*, 1 millimeter in

[1] In order to secure uniformity in the results of tests for the time of setting and tensile strength, the manner of mixing above described should be carefully followed. At least one minute is necessary to obtain the desired plasticity which is not appreciably affected by continuing the mixing for several minutes. The exact time necessary is dependent upon the personal equation of the operator. The error in mixing should be on the side of overmixing.

diameter, 6 centimeters long. The rod is reversible, and can be held in any desired position by a screw *E*, and has midway between the ends a mark *F* which moves under a scale (graduated to millimeters) attached to the frame *A*. The paste is held in

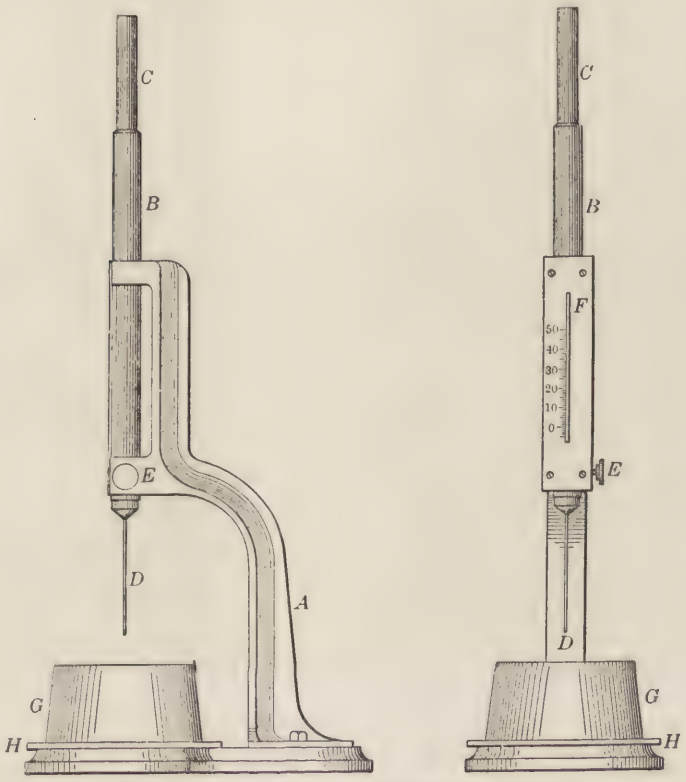


Fig. 168.—Vicat apparatus for determining setting time and normal consistency.

a conical, hard-rubber ring *G*, 7 centimeters in diameter at the base, 4 centimeters high, resting on a glass plate *H* about 10 centimeters square.

39. *Method.*—In making the determination, 500 grams of cement, with a measured quantity of water, shall be kneaded into a paste, as described in Section 36, and quickly formed into

a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained about 6 inches apart; the ball resting in the palm of one hand shall be pressed into the larger end of the rubber ring held in the other hand, completely filling the ring with paste; the excess at the larger end shall then be removed by a single movement of the palm of the hand; the ring shall then be placed on its larger end on a glass plate and the excess paste at the smaller end sliced off at the top of the ring by a single oblique stroke of a trowel held at a slight angle with the top of the ring. During these operations care shall be taken not to compress the paste. The paste confined in the ring, resting on the plate, shall be placed under the rod, the larger end of which shall be brought in contact with the surface of the paste; the scale shall be then read, and the rod quickly released. The paste shall be of normal consistency when the rod settles to a point 10 millimeters below the original surface in one-half minute after being released. The apparatus shall be free from all vibrations during the test. Trial pastes shall be made with varying percentages of water until the normal consistency is obtained. The amount of water required shall be expressed in percentage by weight of the dry cement.

40. The consistency of standard mortar shall depend on the amount of water required to produce a paste of normal consistency from the same sample of cement. Having determined the normal consistency of the sample, the consistency of standard mortar made from the same sample shall be as indicated in Table LXIII,[1] the values being in percentage of the combined dry weights of the cement and standard sand.

Determination of Time of Setting

45. The following are alternate methods, either of which may be used as ordered:

46. *Vicat Apparatus.*—The time of setting shall be determined with the Vicat apparatus described in Section 38. (See Fig. 168).

47. *Vicat Method.*—A paste of normal consistency shall be molded in the hard-rubber ring *G* as described in Section 39, and

[1] See page 642 for table giving percentage of water for sand mortars.

placed under the rod *B*, the smaller end of which shall then be carefully brought in contact with the surface of the paste, and the rod quickly released. The initial set shall be said to have occurred when the needle ceases to pass a point 5 millimeters above the glass plate in one-half minute after being released; and the final set, when the needle does not sink visibly into the paste. The test pieces shall be kept in moist air during the test. This may be accomplished by placing them on a rack over water contained in a pan and covered by a damp cloth, kept from contact with them by means of a wire screen; or they may be stored in a moist closet. Care shall be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point may increase the penetration. The time of setting is affected not only by the percentage and temperature of the water used and the amount of kneading the paste receives, but by the temperature and humidity of the air, and its determination is therefore only approximate.

48. *Gillmore Needles.*—The time of setting shall be determined by the Gillmore needles. The Gillmore needles should preferably be mounted as shown in Fig. 169.

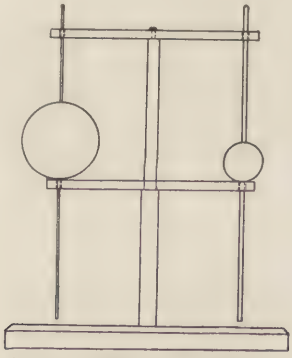


Fig. 169.—Gilmore Needles for determining setting time.

Fig. 170.—Test-piece for use with Gilmore needles.

49. *Gillmore Method.*—The time of setting shall be determined as follows: A pat of neat cement paste about 3 inches in diameter and one-half inch in thickness with a flat top (Fig.

170), mixed to a normal consistency, shall be kept in moist air at a temperature maintained as nearly as practicable at 21° C. (70° F.). The cement shall be considered to have acquired its initial set when the pat will bear, without appreciable indentation, the Gillmore needle one-twelfth inch in diameter, loaded to weigh one-fourth pound. The final set has been acquired when the pat will bear without appreciable indentation, the Gillmore needle one-twenty-fourth inch in diameter, loaded to weigh 1 pound. In making the test, the needles shall be held in a vertical position and applied lightly to the surface of the pat.

Notes

Foreign Specifications for Setting Time

Both the English and German standard specifications call for the use of the Vicat needle. The German specifications prescribe that "normal" Portland cement shall not receive its initial set in less than one hour, and fix no period within which the final set shall take place. The English standard specifications divide cement into three grades, "Quick," "Medium" and "Slow." The requirements for the three are as follows:—*"Quick,"* initial setting time not less than two minutes, final setting time not less than ten, nor more than thirty minutes; *"Medium,"* initial setting time not less than ten minutes, final setting time not less than thirty minutes nor more than two hours; *"Slow,"* initial set not less than twenty minutes, final setting time not less than two, nor more than seven hours. The French Specifications require the cement to have an initial set of not less than twenty minutes and a final set of not less than three hours for cement to be used in sea-water or two hours for cement to be used in fresh-water, or more than twelve hours for both classes.

The determination of the time of setting is only approximate, being materially affected by the temperature of the mixing water, the temperature and humidity of the air during the test, the percentge of water used, and the amount of molding the paste receives.

The cheapest form of moist closet consists simply of a wooden box provided with a door and shelves and painted on the inside

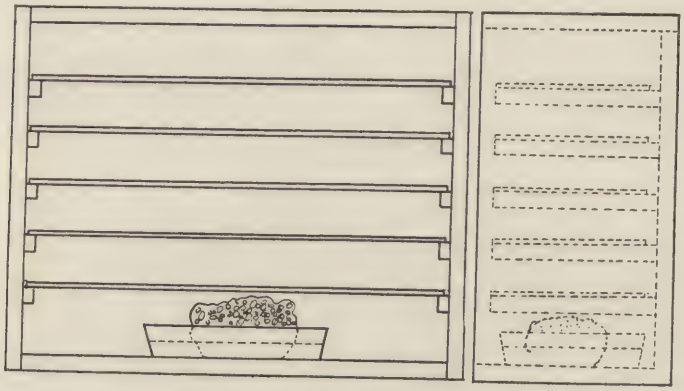


Fig. 171.—Cheap form of moist closet.

with black asphaltum varnish or other good water-proof paint (see Fig. 171). In the bottom of this box should be placed a tin pan containing a sponge, and water should always be kept in this pan. The shelves should be removable and may be made of plate-glass or wood. The shelves should be so placed as to allow a free circulation of air through all parts of the closet. Instead of being painted the box may be lined with thin sheet zinc.

A common tin bread-box makes a very good moist closet where only a few pats and briquettes have to be tested. This is provided with a few cleats and a perforated tin shelf is made to fit into the box, and rests on these cleats. Water is poured into the bottom to a depth of a half inch and the test pieces are placed on the shelf. In order to prevent rusting, this box also should be painted inside with black asphalt varnish.

In large laboratories moist closets made of soapstone have been employed. Such a closet, used in the Municipal Laboratories of the city of Philadelphia, is shown in Fig. 172. This closet is made of one and one-fourth inch soapstone (with the exception of the doors, which are made of wood covered with

zinc) and is in two sections for the reason that it was found that as the height of the closet was excessive, the humidity varied considerably between top and bottom. On the sides of each closet are fastened cleats to hold the shelves, which are of glass or wood.

Mr. Ernest B. McCready described in the Proceedings of the American Society for Testing Materials, Vol. VII, a moist closet

Fig. 172.—Moist closet of soapstone.

made of cement which is employed in his laboratory. Such a closet can be constructed in any cement testing laboratory from waste cement, the forms being made by a local carpenter. A 1 to 2 sand mortar was used and the walls reinforced with one-half inch mesh galvanized wire netting.

Other Methods

The test proposed by General Gillmore, U. S. A., for determining setting properties is the one most used in this country. (See Sections 48 and 49 of Standard Specifications).

The Gillmore needles, or wires, are much more convenient to use where many samples have to be tested, as the pats themselves do not have to be lifted from the moist closet or table, in order to

apply the needle. While the Vicat needle unquestionably is a much more scientific instrument and should be used where great nicety is required in making the test, as in settling disputes, etc.; still for ordinary inspection work, where all that is needed is the assurance that the cement will not set before it is laid in position in the job, and that after it is so placed it will harden in a reasonable time, the simpler and less expensive Gillmore needles will answer the purpose just as well as the more expensive Vicat apparatus. The Gillmore needles are the ones generally used by both manufacturrs and engineers in determining the setting time of cement, and most of those called upon to test and use cement are familiar with the terms initial, and final set as defined by these needles. Setting time is influenced by so many things besides those over which the Vicat needle has control, that the personal equation is as much an element in determinations made with this apparatus as in those made with the Gillmore needles.

The "ball" test for determining the proper consistency is much used in commercial laboratories, using the Gillmore needles to determine set, and in spite of its crudeness, gives results which agree fairly well with those determined by the Vicat apparatus. It consists in forming the mortar into a ball and dropping it from a height of one foot. This fall should not materially flatten nor crack the ball, the former denoting too much water in the mortar and the latter not enough.

In most plant laboratories, and indeed in many testing laboratories where Gillmore's needles are used, it is the practice to test the setting time of cement upon a smaller batch of mortar than that prescribed by the standard rules. Often the same test piece which is employed for setting time is used to determine soundness also (see Chapter XXIII). This plan consists in weighing out from 50 to 100 grams of cement. This is placed upon the mixing slab and a smaller crater is formed in the center of this. The water is next added in a measured amount. The cement is rolled into the crater and the mixture is worked back and forth with a trowel until the proper plasticity is secured. The working usually takes from one to three minutes depending upon the operator and the quickness of his movements. The

cement is then formed into a small cake which is placed on a small glass plate (about 4 by 4 inches) and flattened out with the trowel as shown in Fig. 173, so as to present a smooth surface to the needle. If the pat is also to be used for the steam test, it is drawn out to a thin edge as shown in Fig. 170. For this latter test the pat is allowed to stand in the moist closet, after

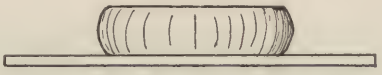


Fig. 173.—Test piece often employed for determining setting time.

the setting time has been taken, until the next day, when it is boiled or steamed.

Observations on Setting Time

The rapidity with which cement sets furnishes us with no indication of its strength. The test is usually made to determine the fitness of the material for a given piece of work. For example, in most submarine work a quick-setting cement is desired, that is, a cement which loses its plasticity in less than half an hour, while for most purposes where sufficient time will be given the cement to harden before being brought into use, a slow-setting cement will usually answer better, or one that sets in an hour or more. The slow-setting cements can be mixed in larger quantities than the quick-setting ones, and do not have to be handled so quickly, so that for most purposes where permissible they are used.

When cement sets hard a few minutes after the mortar is mixed it is said to have a "flash" set. Some cements are so quick setting that they even set up under the trowel and on working get dryer instead of more and more plastic.

Factors Influencing the Rate of Setting

The rate of set is determined by a number of things, chief of which are temperature and the percentage of water used in making the mortar:—The higher the temperature the quicker

the set and the larger the percentage of water the slower the set. Temperature has a very marked influence, and many cements which are suitable for use in this country could not be used in the tropics. Similarly in the early spring and late fall when the temperature out of doors is from 20° to 30° F. below that indoors, cement which tests quick setting in the laboratory may give perfect satisfaction when used at the outside temperature. This influence is shown by the results given below:

TABLE LI.—INFLUENCE OF TEMPERATURE ON THE RATE OF SETTING OF PORTLAND CEMENT.

Temp. °F.[1]	Sample No.	1		2		3		4	
		H.	M.	H.	M.	H.	M.	H.	M.
35	Initial set	3	0	5	0	2	0	2	10
	Final set	8	0	10+	..	6	0	6	0
45	Initial set	1	5	3	0	1	15	1	5
	Final set	3	15	7	30	3	30	3	15
60	Initial set	0	30	2	30	0	15	0	3
	Final set	1	10	6	0	1	0	0	10
80	Initial set	0	4	2	00	0	2	..	..
	Final set	0	10	5	30	0	5	..	..
100	Initial set	..	..	0	45	..	..	..	..
	Final set	..	..	3	10	..	..	..	..

[1] Of room during setting time and of cement and of water used to gauge pats.

The percentage of water used to gauge the pats, or in actual work to make the mortar, affects the setting time, as well as the early strength of the concrete, very greatly. A wet mixture sets very slowly, while a dry one sets much more promptly. In the manufacture of hollow building blocks, where the piece must be removed from the molds at once, only as small a quantity of water as is actually needed to do the work is used, and the mixture of about the consistency of damp sand is rammed into the molds; while in some forms of concrete construction, the mortar is made decidedly plastic, and may be actually poured into the forms. It is then left several days to harden before the latter

are removed. Below are given some results on the effects of various percentages of water on the setting time of Portland cement:

TABLE LII.—Influence of Various Percentages of Water Used to Gauge the Pats on the Setting Time of Portland Cement.

Per. centage of water	Sample No.	1		2		3		4	
		H.	M.	H.	M.	H.	M.	H.	M.
14	Initial set	0	10	2	10	0	10	0	25
	Final set	2	45	6	0	0	35	0	55
16	Initial set	0	20	2	20	0	10	0	25
	Final set	3	50	6	0	0	35	1	0
18	Initial set	1	5	2	20	0	10	..	35
	Final set	5	0	6	15	0	35	1	15
20	Initial set	2	10	2	40	0	8	1	25
	Final set	6	20	6	15	0	30	4	0
22	Initial set	4	20	3	0	0	5	2	15
	Final set	8	0	6	50	0	30	5	0
24	Initial set	5	10	5	0	0	20	3	0
	Final set	12+	..	8	30	0	50	6	10

Another factor which influences very greatly the rapidity of the set of cement is the humidity or the amount of water vapor contained in the air. It has been found that cement will always set much more slowly in a moist closet than it will when left in the open air and for this reason test pieces upon which the setting time is to be made, should always be kept in a moist closet and should not be allowed to remain for more than a minute at any one time out of this.

Rise in Temperature During Setting

It was formerly the practice to determine the rise in temperature during setting, any considerable increase being considered as indicative of free lime in the cement, the supposition being that the rise is caused by the heat formed by the hydration of

the lime. No conclusion could be more erroneous. From the examination of many samples of Portland cement, every detail of whose manufacture was known, I am not afraid to say positively, that the rise of temperature during setting is not only *not* indicative of free lime, but usually comes from the reverse, not enough lime. Those cements which show the greatest increase in temperature during the process of setting are usually the quick-setting cements. These cements usually are low in lime and burned very hard. Many samples of such cements show a rise of temperature distinctly perceptible to the hand, and yet boiling for many hours will fail to distintegrate the pat or warp or check it in any manner. In many instances, the addition of a small quantity (½ per cent) of finely ground lime or 1 or 2 per cent of slaked lime will slow the setting of the cement and in this case no rise of temperature will be met with, showing that the presence of free lime is not the cause of the rise in temperature during setting. On the other hand many samples which fail badly after even a few hours of the steam test, show no greater rise in temperature than the normal. When there is a considerable rise in temperature during the setting of a slow-setting cement, something is probably wrong with the cement, but when the rise is met with, in connection with quick set, it is no evidence of free lime, and the conclusion that it is, is unwarranted by facts.

In this connection, it is well to remark that practically all of the silicates and aluminates of lime met with in cement clinker give off heat when mixed with water and during the process of hydration. The tricalcium aluminate under this condition gives off so much heat that the mass actually boils.

Influence of Sulphates on Setting Properties

If Portland cement clinker is ground just as it comes from the coolers, without the addition of any foreign substance, the resulting cement is entirely too quick-setting to allow of its being properly worked. It is therefore the general practice to either grind a small percentage, usually 2 or 3 per cent of gypsum with the clinker or else to add to the cement just before it is shipped, a corresponding percentage of finely ground plaster of Paris, in

order to regulate the set so as to give time for working, tamping and troweling. At some mills coarsely ground plaster of Paris or calcined plaster as the manufacturers call it, is added to the clinker before grinding.

Le Chatelier made many experiments on the effect of the addition of gypsum and plaster of Paris to Portland cement. He concluded that the governing action which it exercised over the cement was due to the formation of certain soluble compounds between the sulphuric acid of the calcium sulphate and the very active calcium aluminates of the cement which cause quick-setting. He also stated that either gypsum or plaster of Paris could be added to slow the set and that the addition could be made either before or after burning. Since, however, calcium sulphate is decomposed at temperatures decidedly below that at which Portland cement is burned there would be a decided disadvantage, owing to loss of SO_3, in adding gypsum before burning. Indeed from experiments made by the writer if all the sulphur entering the kiln came out with the clinker as calcium sulphate there would be no need to add either gypsum or plaster of Paris.

In spite of Le Chatelier's experiments, it has been a theory generally held in this country that gypsum would not retard the set of cement, but that the only form of sulphate of lime which would do this is plaster of Paris; and that where gypsum is ground in with the clinker, this is transformed into plaster of Paris, the heat generated during grinding being sufficient to drive off the water and make the change from $CaSO_4.2H_2O$ to $(CaSO_4)_2H_2O$. It is true that in many cases the heat generated by the friction of the grinding machinery is sufficient to drive off the water, as the writer has frequently tested cement fresh from the tube mill and found it over 130° C., the temperature at which gypsum loses three-quarters of its water of crystallization. Indeed Shenstone and Cundall state that gypsum begins to lose its water of crystallization at 70° C. in dry air.

To test these various contrary theories and statements the writer and his assistant, Mr. W. P. Gano, carried out the following experiments:[1]

[1] Meade and Gano, *Chemical Engineer*, I, 2, p. 92.

A sample of cement was prepared by grinding fresh normal clinker in the usual way without the addition of any retarder. To separate portions of this were added in different percentages finely ground—

(1) Plaster of Paris, $(CaSO_4)_2.H_2O$, containing 53.18 per cent SO_3.

(2) Gypsum $CaSO_4.2H_2O$, containing 44.22 per cent SO_3.

(3) Dead burned gypsum, $CaSO_4$, containing 55.21 per cent SO_3.

The results are given in the tables below:

The first column shows the percentage of gypsum, etc., added to the cement. By percentage is not meant the percentage of gypsum in the mixture, but the percentage of the weight of cement of gypsum which is added. For instance, 2 per cent means 2 grams of gypsum added to 100 grams of cement, etc.

The second column shows the percentage of water used for the pat, being the amount necessary to obtain a mortar of normal consistency, as determined by the ball test. The third column shows the "initial set" or the time necessary for the cement to harden sufficiently to bear the light Gillmore wire, one-twelfth inch in diameter, loaded with one-fourth pound. The fourth column shows the "final set" or the time necessary for the cement to harden sufficiently to bear the heavy Gillmore wire, one-twenty-fourth inch in diameter, loaded with one pound.

TABLE LIII.—SHOWING THE EFFECT OF PLASTER OF PARIS ON THE SETTING TIME OF CEMENT.

Percentage of plaster of Paris added	Percenage of water used to make pats	Initial set		Final set	
		Hours	Minutes	Hours	Minutes
0	25	0	2	0	6
0.5	23	0	5	0	10
1.0	23	0	50	4	0
1.5	23	2	50	6	0
2.0	22	3	0	6	15
3	22	1	45	5	20
4	22	0	35	4	0
5	22	0	16	2	0
10	22	0	16	1	30
20	22	0	9	0	20

TABLE LIV.—Showing the Effect of Gypsum on the Setting Time of Cement.

Percentage of gypsum added	Percentage of water used to make pats	Initial set		Final set	
		Hours	Minutes	Hours	Minutes
1	23	0	2	0	10
2	23	2	40	5	50
3	22	2	50	5	50
5	22	3	15	6	00
10	22	3	0	5	40
20	22	3	20	6	00

Referring to the tables it will be seen that there is little choice in the three forms of calcium sulphate so far as efficiency goes, all doing the work of retarding the set about equally well. This is to be expected. If the retardation is due to chemical action there is no reason why any one of the three forms should not be as efficient as the others, because they all have approximately the same solubility, that of 1 part in 400-500 parts of cold water. The solution of any of the four would merely be one of a mixture of two kinds of ions, CaO and SO_3, and the SO_3 anions would be as free to react on the aluminates of lime if their source was gypsum as they would if they came from plaster of Paris.

TABLE LV.—Showing the Effect of Dead Burned Gypsum on the Setting Time of Cement.

Percentage of burned gypsum added	Percentage of water used to make pats.	Initial set		Final set	
		Hours	Minutes	Hours	Minutes
1	23	0	6	0	10
2	23	1	45	5	10
3	23	1	47	5	30
5	23	2	0	5	30
10	23	1	50	5	0
20	23	2	20	5	0

It will be noticed, by reference to Table LIII, that 2 per cent plaster of Paris produced the maximum retardation of the set. Larger quantities than this had the effect of quickening the set of the cement. This maximum of course varies with different cements, but with all it will be found that there is a point beyond which additions of plaster will be attended with shortening instead of further lengthening the setting time of the cement.

As we have said many manufacturers prefer to add plaster of Paris to cement just before it is shipped. If it is properly mixed with the cement there are certainly points in favor of adding the sulphate here. We do not see, however, why finely ground gypsum would not do the work just as well, saving the cost of calcining. On the other hand if the gypsum is added to the clinker, it is sure to be finely ground and thoroughly disseminated throughout the cement, two things necessary with any form of sulphate, if it is to act as a retarder. There will be no danger of the gypsum failing to do its work, whether the temperature is low or high during grinding, because dehydration is not necessary. It must be remembered, however, that plaster of Paris contains more sulphuric acid than gypsum, 290 parts of the former being equivalent to 344 of the latter or a ratio of 87 : 100 so that plaster of Paris weight for weight is the more effective of the two.

Influence of Calcium Chloride on Setting Time

Another substance which will retard the setting of cement is calcium chloride, though the writer has never heard of its being used in practice. Candlot made many experiments upon the effect of chloride of calcium on the setting of ground cement clinker. Below are some of his results:

TABLE LVI.—INFLUENCE OF CALCIUM CHLORIDE ON THE SETTING TIME OF PORTLAND CEMENT.

Solution of $CaCl_2$ Gr. per liter	1 h. m.	2 h. m.	3 h. m.	4 h. m.
2	0.05	1.05	8.00	1.34
5	0.08	10.00	12.00	2.00
10	8.18	10.00	14.00	5.50
20	1.00	12.00	10.30	8.00
40	4.35	8.00	6.30	8.35
60	3.20	6.00	4.00	6.00
100	0.03	0.20	0.30	3.30
200	0.03	0.09	0.05	0.25
300	0.02	0.08	0.03	0.05

Carpenter[1] also made some experiments on grinding the clinker and calcium chloride together. His results are given below and show that chloride of calcium has effect in retarding the time of setting and exerts the greatest effect when about one-half of 1 per cent by weight of the chloride of calcium is employed:

[1] Sibley, *Journal of Engineering* (Cornell University), January, 1905.

TABLE LVII.—Influence of $CaCl_2$ Ground Dry with the Clinker.

Per cent of $CaCl_2$	Per cent of water	Initial set minutes	Final set minutes
0.0	29.8	115	274
0.5	34.1	160	272
1.0	29.8	167	234
1.5	26.4	127	212
2.0	25.4	103	180
2.5	26.4	45	182
3.0	26.4	97	185
3.5	26.4	63	150
4.5	28.6	73	160
5.0	29.8	76	84
5.5	29.8	68	145
6.0	29.8		

Influence of Hydration

Various authorities have at different times suggested the possibility of retarding the set of cement by the use of water alone or with gypsum. Ware[1] states that in his experience he found that a certain lot of seasoned clinker also low in lime which under normal conditions gave quick-setting cement when ground either alone or with gypsum would give normal cement when ground under conditions which would permit of hydration. He found that it made little difference how the water was added. He tried the following methods all of which were successful.

(1) The clinker was ground hot, the heat liberating the water from the gypsum.

(2) Water was sprinkled on the cold clinker.

(3) Steam was turned into the conveyor leading from the mills. The method finally adopted was to heat the clinker and grind while still hot with gypsum which had been thoroughly wetted.

Ware also stated that in the laboratory quick-setting cement could often be made slow setting by simply dropping it through a 30-inch vertical tube through which a cloud of steam was rising. He also succeeded in making quick-setting cement normal by rapidly mixing by hand 3 per cent of water with the ground cement and then grinding in a laboratory pebble mill for a short time in order to further mix it.

[1] Ware, *Concrete-Cement Age*, April, 1913.

Bambier found he could slow the setting time of cement by passing superheated steam into the tube mill by means of a pipe inserted through the head. The writer has had some experience with this method as it was tried at one mill with which he was associated. It does cut down to some extent the amount of gypsum required but at this mill the results obtained indicated that the method was not reliable where no gypsum was used. The practice is of value, however, in curing unsound cement.

Quickening the Setting Time

Certain reagents if added to cement have the property of quickening the set of the latter. The alkalies have this property to a marked degree. Even a small percentage of sodium carbonate added to cement will quicken the set of the latter quite appreciably. Commercial "soda ash" is crude sodium carbonate and where it is desired to hasten the set of cement, this chemical is usually employed. There are some objections to its use, however, chief of these are the absence of any authoritative research work to show the effect of such additions on the strength and permanency of the resulting concrete. The alkali is also likely to appear as an efflorescence on the surface of the concrete.

Effect of Storage of Portland Cement on Its Setting Properties

No property of Portland cement is harder to control than its "set," or gives the manufacturer more trouble. This is not so much because of any difficulty in the way of making a slow-setting cement, as it is of making one which will stay slow-setting under all ordinary conditions of storage and aging. Every manufacturer can cite instances of cement which left the mill having the proper setting time, and yet which turned up at the job with a "flash" set. Bins of freshly made cement will frequently test slow-setting and yet, after seasoning some weeks, will show quick set on again testing.

The converse of this is also true, some cements which, when freshly made are quick-setting, will in time become slow-setting, and again slow-setting cements may become quick-setting and then slow-setting again. As a usual rule a cement which is slow-

setting when freshly made and which becomes quick-setting on storage is under-limed, and the trouble can usually be remedied by increasing the percentage of lime in the cement. High-limed, well-burned and made cements do not usually show this fault. What percentage of lime it is necessary to carry in order to avoid this trouble is a question every mill must decide for itself, but, in general, it may be said that cements high in alumina will require a high percentage of lime to overcome this fault, and in some instances the margin between the minimum of lime to insure against quick set and the maximum allowed by a good hot test is very narrow.

The table below illustrates the changes in the setting time of cement, due to aging.

TABLE LVIII.—INFLUENCE OF AGING OF THE SET OF PORTLAND CEMENT.

Sample No.		1		2		3		4		5		6		7	
		H	M	H	M	H	M	H	M	H	M	H	M	H	M
Fresh.....	Initial set	2	50	3	10	4	10	2	40	·	2	·	10	·	4
	Final set	6	0	6	40	8	0	6	15	·	15	·	25	·	10
1 week old...	Initial set	1	30	..	10	2	15	·	3	·	2	·	5	·	4
	Final set	4	10	..	25	6	0	·	8	·	10	·	15	·	10
2 weeks old..	Initial set	0	3	..	5	1	25	·	3	·	15	·	30	·	4
	Final set	0	7	..	11	3	40	·	8	·	35	1	5	·	10
4 weeks old..	Initial set	0	3	..	5	·	30	·	5	1	30	1	50	·	15
	Final set	0	7	..	15	1	50	·	11	4	10	4	45	·	30
3 months old.	Initial set	·	30	..	4	·	10	·	3	1	35	2	0	2	40
	Final set	1	15	..	15	·	30	·	8	4	0	6	10	6	5
6 months old.	Initial set	·	25	..	20	·	..	·	3	2	10	2	0	2	10
	Final set	1	15	1°	10°	·	..	·	8	6	0	6	10	5	40
1 year old....	Initial set	·	25	..	55	2	20	·	4	2	0	1	40	2	15
	Final set	1	10	2	30	5	45	·	10	5	30	5	5	6	5

The reason commonly given for the quickening of the set of Portland cement is that the plaster of Paris $(CaSO_4)_2H_2O$, has hydrated and reverted to gypsum, $CaSO_4.2H_2O$. It is a fact, however, as is generally well known, and as we have mentioned before that gypsum is practically as efficacious a retarder as plaster of Paris. Not only will the mineral gypsum slow the set of cement but the artificial gypsum, formed when plaster hydrates or sets, will also act in the same manner, as the following results will show.

TABLE LIX.—THE EFFECT OF "SET" PLASTER OF PARIS ON THE SETTING TIME OF CEMENT.

Percentage of "set" plaster of Paris added	Percentage of water used to make pats	Initial set		Final set	
		Hours	Minutes	Hours	Minutes
0	25	0	2	0	6
1	23	0	8	0	40
2	23	1	45	5	0
3	23	2	0	5	20
5	23	1	45	6	0
10	23	1	55	5	35
20	23	2	15	5	50

In view of the fact that both gypsum and set plaster of Paris, which is merely plaster of Paris reverted into gypsum, will slow the set of cement, there can be nothing in the theory that plaster loses in time its control, over cement, for the only change which the plaster can undergo is to absorb water from the air forming gypsum. We must therefore seek for another solution of the matter. Mr. Clifford Richardson suggested one, in his paper on the "Constitution of Portland Cement," read before the Association of Portland Cement Manufacturers, at Atlantic City, June, 1904. His theory being that the tension in the solid solution of calcium silicates and aluminates, which constitutes cement, is released by changes in temperature, etc., setting free some aluminate which makes the cement quick-setting again.

Against this latter theory are several facts, chief of which is that cements kept in air-tight vessels do not get quick-setting. The writer has many times divided a sample of cement, which from its analysis led him to believe it would develop a "flash" set on aging, into two portions, storing one in a small paper bag and the other in an air-tight fruit jar, and, in no case, has he ever observed the sample in the jar to become quick-setting, although in most cases that in the bag developed an initial set of from two to ten minutes after a week's time. In making this test three pats were always made of each sample, both before and after aging, and the bag and jar were placed side by side on the shelf, where both would be subjected to the same changes of temperature, etc.

Influence of Slaked Lime on Setting Time

When cement has become quick-setting from storage it can generally be made slow-setting again by simply adding 1 or 2 per cent of slaked lime, or by gauging the pat with lime-water. This seems to lead to the conclusion advanced by Candlot that the quickening of the set of cement on exposure to air is due to the change of the small percentage of free or of hydrated lime always present in cement to the inert carbonate. This change is brought about by the carbon dioxide of the air, consequently, when not exposed to the air, the cement does not become quick-setting. Slaked lime will not itself slow the setting of unsulphated cement, and calcium sulphate must be present in some form or other, so that it is probably a mixture of calcium sulphate and calcium hydrate which retards the hydration of the aluminates, and consequently the activity of the cement.

Cement which has become quick-setting may also be made slow-setting again by addition of a small percentage of plaster of Paris. One-half of 1 per cent is usually sufficient for this purpose. When bins of cement have become quick-setting, from age, it is usual to bring the setting time back to normal by such means. Usually a square box made to hold so much plaster of Paris (when struck off level) is added to every barrow of cement as it is wheeled from the bin to the conveyor, or else a box is dumped into the conveyor at stated intervals of time. The screw conveyor then does the mixing and usually does it pretty thoroughly, too. Some mills are provided with automatic scales and mixers for doing this work, but these are usually installed only in those mills which use plaster of Paris and make the addition before packing, instead of grinding gypsum in with the clinker.

Quick-setting cements may also be rendered slow-setting by mixing them with slow-setting ones, but this must be carefully done to see that both bins are drawn from in the desired proportions.

The property slaked-lime has of slowing the setting time of cement which has quickened with age does not seem to be utilized as much as it might be. I know of one cement mill where

hydrated lime was added for a short time for this purpose and of another which contemplated doing so. Most manufacturers, however, have found it simpler to add a little more plaster of Paris to such cement as becomes quick-setting, just before it is packed and so bring back its setting time to the normal. The contractor or engineer, however, might in many cases add hydrated lime to the cement and so relieve the manufacturer of the expense of taking the cement back to the mill in order to plaster it. On small jobs, where water is added to the concrete from barrels, the addition of a few lumps of lime to the contents of the barrel would make the cement slow-setting, and the resulting concrete would be as strong as if no lime had been added. Sidewalk makers and other users of cement who do not test their purchases may safeguard themselves against using quick-setting cement unawares by the use of lime in this way or by mixing hydrated lime with the mortar.

Manufacturing Conditions Effecting Setting Time

Theoretically, the setting time of cement should be controlled by the amount of gypsum added. From a perusal of the preceeding paragraphs, however, it will be apparent that other conditions will influence this materially. The specifications allow as much as 2 per cent sulphur trioxide in the cement. Cement clinker burned with coal ordinarily contains from 0.3 to 0.5 per cent sulphur trioxide and gypsum when pure 46 per cent of this constituent; so ordinarily the maximum amount of pure gypsum which can be added without having the cement exceed the limits of the specifications is 3.4 to 3.8 per cent of the weight of the clinker (12½ to 14½ pounds per barrel of cement). It has been found that unless the clinker is of proper chemical composition and has been properly burned it is not possible to slow the set of the resulting cement to the requirements of the specifications with this amount of gypsum.

The influence of both alumina and lime on the setting time of cements has been pointed out in Chapter II of this book. Generally speaking cements high in alumina are apt to be quick-

setting or to become so when aged. On the other hand, high silica cements are not so likely to show this tendency.

The percentage of lime in the cement has a marked influence on its setting time. High limed and well burned cements made from finely ground raw materials are slow setting after a moderate amount of gypsum has been added, nor do they usually become quick-setting on aging. What percentage of lime it is necessary to carry at any individual works in order to avoid quick-setting cement is a question each mill must find out for itself, but in general it may be said that cements in which the ratio $CaO : SiO_2 + Al_2O_3 + Fe_2O_3$ is two or better will be satisfactory. Cements high in alumina will require a high percentage of lime to overcome the tendency to become quick-setting and in some instances the margin between the minimum of lime to insure against quick set and the maximum allowed by a good hot test is very narrow. It is particularly desirable that the clinker be uniform in composition. Low lime clinker mixed with high lime material may apparently be of satisfactory chemical composition, due to averaging, and yet the influence of the low lime material will be sufficient to make the cement quick-setting.

Mixtures of underburned and normal or very hard burned clinker are also apt to be quick-setting, consequently uniform burning is desirable if the set of the cement is to be regular.

When cement is quick-setting or becomes so, even after the maximum amount of gypsum allowable is added, it will generally be found that the trouble can be remedied by increasing the percentage of lime in the cement, by more careful burning and by fine grinding of the raw materials, one or all.

CHAPTER XXIII

SOUNDNESS

Standard Specification and Method of Test

Specification.—A pat of neat cement shall remain firm and hard, and show no signs of distortion, cracking, checking, or disintegration in the steam test for soundness.

Method of Test

41. A steam apparatus which can be maintained at a temperature between 98 and 100° C., or one similar to that shown in Fig. 174, is recommended. The capacity of this apparatus may be increased by using a rack for holding the pats in a vertical or inclined position.

42. A pat from cement paste of normal consistency about 3 inches in diameter, ½ inch thick at the center, and tapering to a thin edge, shall be made on clean glass plates about 4 inches square, and stored in moist air for twenty-four hours. In molding the pat, the cement paste shall first be flattened on the glass and the pat then formed by drawing the trowel from the outer edge toward the center.

43. The pat shall then be placed in an atmosphere of steam at a temperature between 98 and 100° C. upon a suitable support 1 inch above boiling water for five hours.[1]

44. Should the pat leave the plate, distortion may be detected best with a straight edge applied to the surface which was in contact with the plate.

[1] Unsoundness is usually manifested by change in volume which causes distortion, cricking, checking or disintegration.

Pats improperly made or exposed to drying may develop what are known as shrinkage cracks within the first twenty-four hours and are not an indication of unsoundness. These conditions are illustrated in Fig. 175.

The failure of the pats to remain on the glass or the cracking of the glass to which the pats are attached does not necessarily indicate unsoundness.

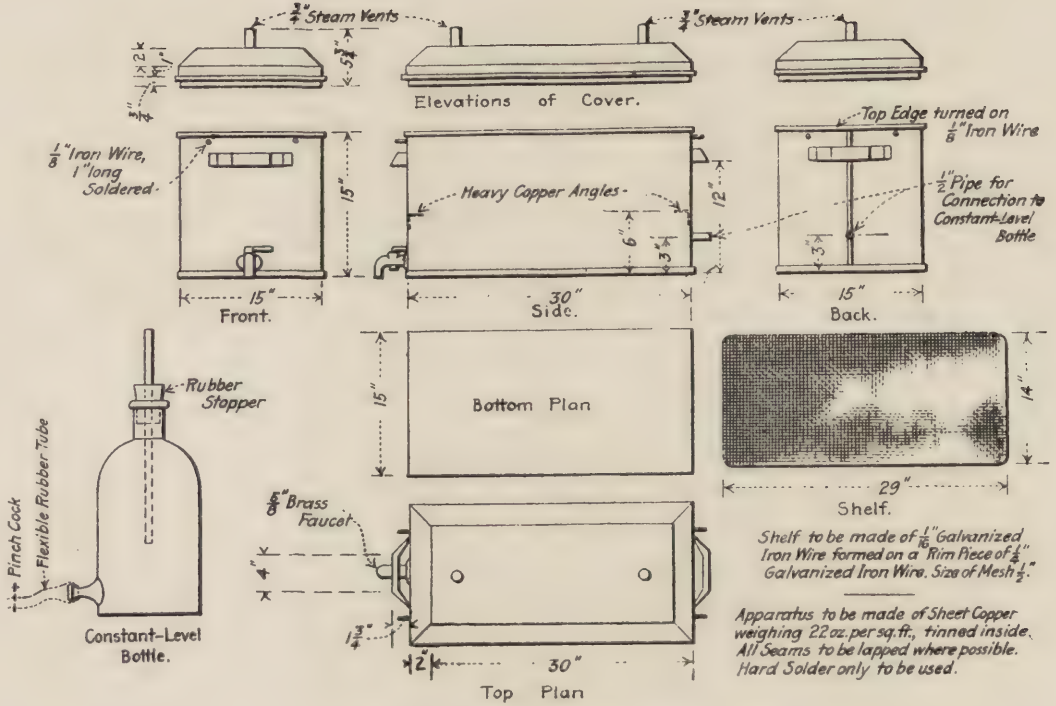


Fig. 174.—Apparatus for making soundness test of cement.

Fig. 175.—Typical failures in soundness test.

Notes

The boiler may be made of any convenient metal. The specifications call for copper tinned on one side, but galvanized iron will make a satisfactory apparatus. The arrangement for maintaining a constant water level in the boiler consists of a bottle with an opening at the bottom as shown in Fig. 176. Through the rubber stopper of this bottle, a glass tube is passed with its lower end on a level with the point in the pat boiler at which it is de-

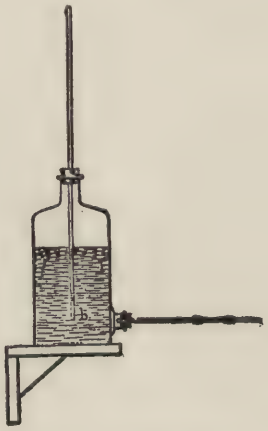


Fig. 176.—Constant water level apparatus.

sired to maintain the surface of the water. Whenever the water in the boiler reaches a point below that of the bottom of the tube, water will flow in from the bottle.

The pat boiler should always have a hole in the cover through which the steam may escape. In some laboratories steam is used to heat the pat boiler and in such instances, as indeed when the boiler is heated by a flame, the opening should be large enough not to permit any pressure in the boiler.

When only a few tests have to be made a convenient form of boiler consists of a common tin bucket provided with a tin top. A small hole to permit exit of the steam is made in the top and a shelf of wire net or perforated tin is placed in the bucket and

supported by any appropriate means at least one inch above the water level. The pats are set on this shelf. A still better pat test apparatus consists of a galvanized iron bucket on the bottom of which rests a perforated pie plate. The pats to be boiled are placed on this and it is also provided with a rack of ¼-inch mesh galvanized wire netting. This rack is stiffened with a wire ring soldered to it and bent up at two places to form a handle. Such a pat boiler will last a long time, stand rough service and permit of the steaming and boiling of four or five pats of cement at one time.

The boiler may be heated by any appropriate means. A gas or oil stove is generally used but an electric hot plate or heating coil built in the boiler will be found most convenient. In making the test be sure the water boils. Sometimes the boilers are heated by a steam coil with live steam under pressure, such an arrangement where steam under 50 pounds or more pressure is available is convenient, except for the difficulty of cleaning the boiler.

Cracks due to disintegration should not be confused with those caused by drying of the pat. The former are wedge-shaped and radiate from the center of the pat, while the latter usually run across the middle of the pat or around its edges. Fig. 176A illustrates the two forms of cracks. *A* is a shrinkage crack and *B* cracking caused by expansion. Shrinkage cracks, due to drying, are usually developed in a day or two and are due to too thin (wet) a paste, to allowing the pat to harden in the air instead of the moist closet or to lack of humidity in the moist closet. Disintegration cracks rarely appear in either air or cold water pats until after two or three days and are due to unsoundness.

The failure of the pats to remain on the glass does not necessarily indicate that the cement from which they are made is unsound. Likewise the cracking of the glass to which the pat is attached during boiling means nothing to condemn the cement and is due merely to unequal expansion of the pat and glass and the firm adhesion of the one to the other.

Pats which are steamed usually disintegrate in a very marked manner where the cement is at all unsound. Usually disintegration is so marked that the pat may be easily crumbled between

the fingers. The first indications of failure are usually the appearance of radial cracks, although not always, and this is followed by more or less checking over the entire surface of the pat. Pats which are sound will usually be found to break between the thumb and finger sharply, with a marked snap, while those which are unsound will more or less crumble. Pats made of sound cement are always hardened by steaming. Those made of unsound cement are weakened.

Pats should always be allowed twenty-four hours to harden before steaming. Sometimes pats will stand the steam test when this is applied before the pat hardens although they would not do this if allowed to remain twenty-four hours before steaming. Again the reverse of this is true.

Other Methods

Normal Tests

Until recently two other tests were required for soundness—the "air test" and the "*cold water test.*" In both instances thin edge pats were made as specified for the stream test. The pat to be subjected to the air test was kept in air at normal temperature and observed at intervals for twenty-eight days. The pat to be subjected to the cold water test was kept in cold water maintained at as near 70° F. as practicable and observed for at least twenty-eight days. The pats to satisfactorily pass the requirements of either test should remain firm and hard and show no signs of distortion, checking, cracking or disintegrating. Should the pats leave the glass plate distortion was detected with a straight edge applied to the surface which was in contact with the plate. Many cements which will not pass the standard steam test will pass these two tests. Until recently the cold water test was considered the "court of last resort."

Boiling Test

This test, originated by Michaelis, is somewhat more severe than the standard steam test and was much employed until recently. It has now been largely superseded by the steam test,

however. As devised by Michaelis, it consisted in rolling the neat cement paste into a small ball and then flattening this into a round cake about one-half inch thick. These cakes were then immediately placed in a vessel of cold water and heat was applied to the latter so that the water was gradually brought up to boiling and the latter continued for three hours. The pats were then examined for checking and cracking.

As used in America, the test was usually made on thin edge pats which had been allowed to harden in moist air for twenty-four hours. At the end of that time, these were placed on a rack in a vessel of cold water, fully submerged in the liquid, and the water gradually brought to boiling. The boiling was usually continued for three to five hours when the pats were removed and examined. The requirements for passing the test were the same as now required for the steam test.

A great many cement testers steam the pat for five hours and then boil them a few hours, the idea being that the boiling will bring out any injurious qualities not shown by the steam test. The boiling test is generally considered the more severe test although the writer's experience has been that the difference between the two tests is not nearly so marked as is generally supposed.

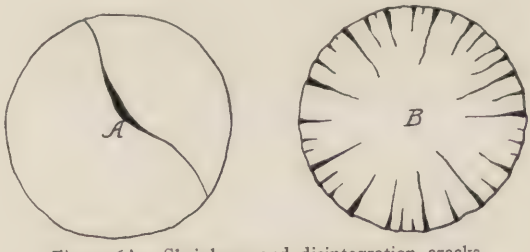


Fig. 176A.—Shrinkage and disintegration cracks.

The boiling test should always be made with fresh water and any accumulation of lime and other sediments in the bottom of the pat boiler should be carefully scraped out each time before filling. Pats should also be supported from the bottom of the boiler so that they do not come in contact with the latter. As

it is easy to see, a pat formed on glass will have a very smooth under side and will come into sufficient close contact with the bottom of the pat boiler to receive the heat directly through the latter and thus have its under side heated to a very much higher temperature than that of the boiling water surrounding it.

German Specifications

The standard German specifications at one time included an accelerated test something like our own steam test. This has been abandoned, however, and the new rules recognize only the cold water test and prescribe that this shall be carried out in the following manner.

Portland cement must be volume constant. It shall be recognized as decisive proof of this when a pat of neat cement, prepared on a glass plate, protected from drying out, and placed under water after twenty-four hours, shows no sign of curvature or cracking on the edge, even after a long time.

For this test the pat made for judging the setting process is, with slow-setting cement, put under water after twenty-four hours, but in any case only after being hard set. With quick-setting cement this can be done after a shorter time. The pats, especially those of slow-setting cements, should be protected from drying out by storing in a covered box until the setting is finished. If the pats, while under water, curve or show cracks on the edge, this indicates undoubted expansion of the cement, *i. e.*, in consequence of the increase of volume disintegration of the cement occurs by gradual loss of coherence, leading to complete crumbling.

The signs of change in volume are generally shown after three days; in any case an observation of twenty-eight days is sufficient.

Le Chatelier Test, British Specifications

The British Standard Specifications require the cement to pass the Le Chatelier test. The apparatus for conducting this test is shown in Fig. 177. It consists of a small split cylinder of spring brass or other suitable metal of 0.5 mm. (0.0197-in.) in thickness.

30 mm. (1.1875-ins.) internal diameter, and 30 mm. high, forming the mold, to which on either side of the split are attached two indicators 165 mm. (6.5-ins.) long from the center of the cylinder, with pointed ends *a*, *a*, as shown upon the sketch.

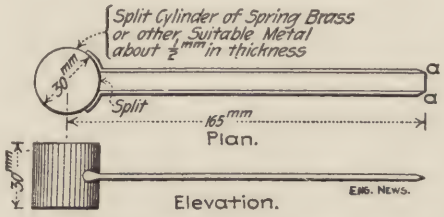


Fig. 177.—Le Chatelier's calipers.

The mold is to be placed upon a small piece of glass and filled with cement gauged in the usual way, care being taken to keep the edges of the molds gently together while this operation is being performed. The mold is then covered with another glass plate, a small weight is placed on this and the mold is immediately placed in water at 58° to 64° F. and left there for twenty-four hours.

The distance separating the indicator points is then measured, and the mold placed in cold water, which is brought to a boiling point in fifteen to thirty minutes, and kept boiling for six hours. After cooling, the distance between the points is again measured, the difference between the two measurements represents the expansion of the cement, which must not exceed the limits laid down in the specification.

The British standard specifications demand that the cement shall not show a greater expansion than 10 mm. after having been spread out for a depth of 3 inches and exposed to the air for twenty-four hours at a temperature of 58° to 64° F. and 5 mm. after seven days such aeration.

French Specifications

The French Specifications also call for the soundness test to be made by the Le Chatelier method and do not seem to permit of

the aeration of the sample of cement. These rules require cement for use in sea water to be tested by boiling in sea water for three hours and allow an expansion of not more than 5 mm. Cement to be used elsewhere is to be boiled in fresh water for three hours and may show a maximum of 10 mm. expansion. The French method allows the test pieces to harden for twenty-four hours in moist air before boiling.

High Pressure Boiling Tests

Various authorities at different times have proposed soundness tests for cement even more severe than the boiling test. These have consisted in either boiling or steaming the test pieces under pressure. Erdmenger,[1] as far back as 1881, proposed the testing of cement in this manner. Erdmenger's test, however, never came into general use in Germany and most German authorities considered it of no value.

Interest in these high pressure tests was revived in 1913 by the proposal of Mr. H. J. Force, in charge of the testing laboratory of the Lackawanna R. R., to include in specifications for Portland cement a high pressure test which consisted in boiling briquettes in an autoclave at a pressure of 295 pounds. The briquettes were then broken for tensile strength. The Force test was quite thoroughly discussed at that time and it was the general concensus of opinion among cement experts that the test was more severe than was required by ordinary building conditions and was of doubtful value even where the requirements were most exacting. As the result of this discussion the test has never come into anything more than very limited use.[2]

The Force test consisted in making three standard neat briquettes in the usual manner and allowing these to harden in moist air for twenty-four hours. The briquettes were then placed in an ordinary autoclave such as is used in chemical laboratories, partly or wholely covered with water and then boiled under a pressure of approximately 295 pounds for two hours. The pressure was gradually released and the test pieces removed. After cooling

[1] *Jour. Soc. Chem. Ind.*, Vol. XII, p. 927.

[2] *Technologic Paper, No. 47*, U. S. Bureau of Standards.

for one hour in a moist closet the briquettes were broken in the ordinary way. Mr. Force, in his specifications required that the cement when tested in this manner should show a tensile strength of at least 500 pounds per square inch and an increase of 25 per cent over the strength obtained from briquettes remaining in moist air for twenty-four hours (Standard neat one-day test).

Mr. Force also made up a bar of neat cement 6 x 1 x 1 inches which he treated just as indicated above for the briquettes. This bar was measured before and after boiling in the autoclave, and was not to show an expansion greater than 1 per cent as the result of this treatment.

Faija's Test

Probably the mildest of the hot tests is that of the English cement expert, Henry Faija. His method consists in subjecting a freshly gauged pat upon a plate of glass prepared as directed

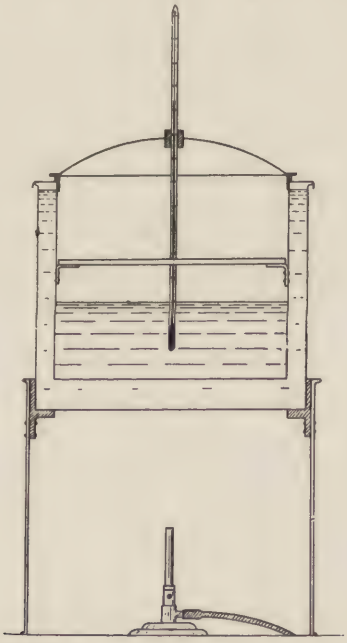


Fig. 178.—Apparatus for Faija's soundness test.

above to a moist heat of 100° to 105° F. for six or seven hours, or until thoroughly set, and then immersing it in water kept at a temperature of 115° to 120° F. for the remainder of the twenty-four hours. For this test he used the apparatus shown in Fig. 178. It consists of a covered vessel in which water is kept at the even temperature of 115° to 120° F. by means of a water-jacket. The inner vessel is filled with water to the height shown. Above the water level is placed a rack. When the water in the inner vessel is at the temperature of from 115° to 120° F., the upper part of the vessel will be filled with aqueous vapor and this latter will be at a temperature of from 100° to 105° F. As soon as the pat is gauged it is put on the rack and left there for six hours. It is then placed in the warm water and allowed to remain eighteen hours longer. To pass the test, a test pat after the above treatment should show no signs of cracking or blowing and adhere firmly to the glass plate on which it was made.

Kiln Test

Dr. Bohme suggested the kiln test. This test was until recently considered as the standard German accelerated test for soundness. It has now, however, been abandoned and the cold water pat test substituted. The test was carried out as follows:

A stiff paste of neat cement and water is made, and from this cakes 8 cm. to 10 cm. in diameter and 1 cm. thick are formed on a smooth impermeable plate covered with blotting paper. Two of these cakes which are to be protected against drying in order to prevent drying cracks, are placed after the lapse of twenty-four hours, or at least only after they have set, with their smooth surface on a metal plate and exposed for at least one hour to a temperature of from 110° C. to 120° C. until no more water escapes. For this purpose the drying closets in use in chemical laboratories may be utilized. To pass this test, the cakes should show after this treatment no edge cracks.

Calcium Chloride Test

Candlot discovered by a series of experiments upon cement that if the cement is either gauged with or kept in water contain-

ing calcium chloride the free lime in it is slaked much more quickly. The more concentrated the solution the more marked the effect. The action of the salt is, therefore, similar to that of heat, to increase the chemical action causing expansion. To carry out the test, gauge the cement with a 4 per cent solution (40 grams to the liter) of calcium chloride, make into pats upon glass plates and allow to set, after which immerse the pats in the cold 4 per cent solution of calcium chloride for twenty-four hours and then remove and examine for cracks, softening, etc.

Bauschinger's Calipers

The expansion or contraction of cement during hardening may be measured directly and very accurately by means of Bauschinger's caliper apparatus (Fig. 179). By means of this instrument changes in the length of small parallelopipedons, 100 mm.

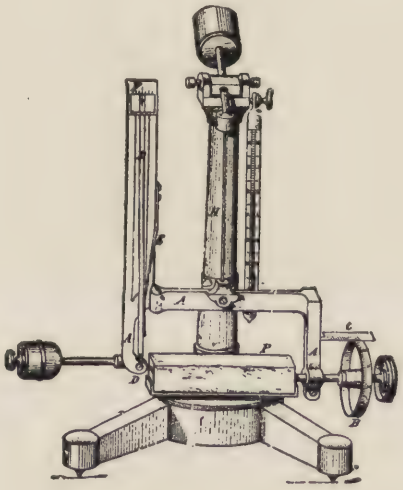


Fig. 179.—Bauschinger's calipers.

long and 5 sq. cm. cross-section, may be actually measured to within 1/200 mm. The apparatus consists of a stirrup-shaped caliper, having a fine micrometer screw on its right arm, the left being the support of a sensitive lever. The shorter arm of this

lever terminates in a blunt caliper point and is pressed against the measuring screw by a spring attached to the long arm. The calipers are readily moved in any direction and the micrometer is read in the usual manner. One revolution of the screw equals 0.5 mm. and the readings on the head are made at 1/200 mm. The specimen is molded with square cavities in the ends, and in these are set plates of glass containing centers for the caliper points. The molding is done similar to that for tension specimens except that both sides should be repeatedly struck off smooth. It requires but a few minutes to measure a specimen by this apparatus.

The writer has used a form of caliper which may be easily made. This consists of an ordinary machinist's micrometer caliper which has been cut in two and extended to six inches by riveting in securely a piece of brass, in order to allow the taking of a prism of this length. The riveting must be so done that the caliper points will not spread when pressure is applied. This is accomplished by having the rivets fit the holes very tightly. The caliper may be used in either of two ways. (a) Pieces of glass plate are placed in the cement prism so as to serve as centers for the caliper points or (b) two small brass screws with round heads to which have been soldered copper wires may be molded in the test pieces and these attached to a battery and sounder. When the caliper points touch the screws on both sides of the prism, electrical connection is established, which causes the sounder to buzz.

Microscopic Test for Free Lime.

Prof. Alfred D. White proposes[1] a microscopic test for free lime. Unfortunately this test does not differentiate between calcium oxide which causes unsoundness and calcium hydrate which is developed in cement on storage and seasoning of either the clinker or the cement itself. As all cement contains calcium hydrate to the extent of from 2 to 5 per cent and even more when it reaches the consumer the test is of no value to the latter to determine unsoundness. In scientific investigations at

[1] *J. Ind. and Eng. Chem.*, Jan., 1909.

the plant on freshly burned and ground clinker the test will be found of some use.

The method is based on the formation on the slide of the microscope of a characteristic crystalline calcium phenolate readily recognizable in polarized light. The reagent is prepared by dissolving crystallized phenol in an immiscible and rather non-volatile solvent and adding a trace of water. The method of preparation preferred by the author is to dissolve 5 grams of phenol in 5 cc. nitrobenzol and add to this solution two drops of water. Instead of nitrobenzol, alpha brom-naphthalene may be used, and is for some reasons, notably its lower volatility, to be preferred. It does not, however, give such sharp results as nitrobenzol.

In making this test about two or three milligrams of the finely powdered material are placed in the center of a microscope slide,

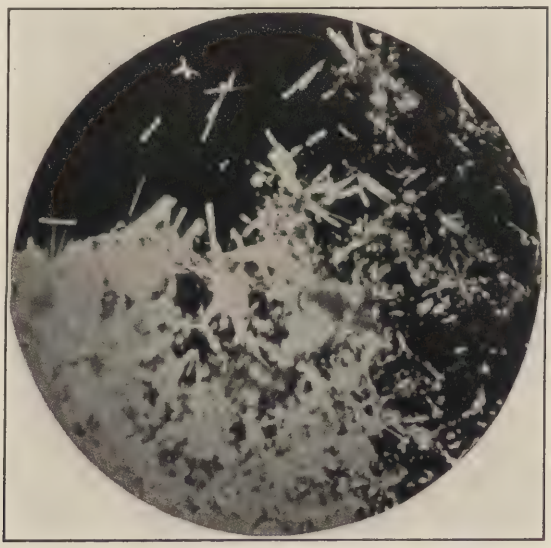


Fig. 180.—Microscopic test for free lime.

a drop of reagent put upon it and then a cover glass, which is pressed down and rubbed gently to and fro till the cement spreads

itself out somewhat. It is advisable not to spread the cement out too thinly but to leave a thick nucleus where the crystals will first appear, and to have the thickness decrease toward the edges. The slide is now observed in a polarizing microscope with the nicols crossed, or if easier for the eye, with the polarizer rotated slightly. Prof. White recommends a two-thirds inch objective and one inch eye-piece giving a magnification of about 80.

The phenomena appearing when pure lime alone is being observed will first be described. When the freshly-prepared slide is put on the microscope the lime being isotropic is almost invisible and the whole field is dark. Within a few minutes the edges of the fragments of lime begin to show brilliant points which in a quarter of an hour develop into brilliant clusters of radiating needles as shown in Fig. 180 which is a photomicrograph of a commercial cement. On account of the great contrast in illumination between the brilliantly refracting calcium phenolate and the feebly refracting cement the photomicrograph shows nothing but the calcium phenolate crystals and does not show these sharply since their strong double refraction makes them appear to be surrounded by a halo. The eye of the observer at the microscope can readily discern the individual crystals forming what are only blotches of white in the photograph. If the lime fragments are crowded too closely together on the slide the crystals interlace so that their structure cannot be noted. These crystals grow till in the course of a couple of hours they may be 0.1 mm. long. Very little further change is noticeable for six hours but in twenty-four hours the nitrobenzol will have largely evaporated and the crystals may have entirely disappeared. Confusion from formation of crystals of phenol has never been observed by White, the moisture present in the reagent or absorbed from the air probably preventing the phenol from crystallizing when the solvent evaporates.

Hydrated calcium oxide gives needles similar to the oxide, but they generally form more rapidly and are finer. On the other hand, the crystals formed from lime which has been fused in the electric arc have a different form. Instead of straight

needles the crystals appear as plumes or feathery petals which in favorable cases give the group somewhat the appearance of a chrysanthemum. Something of this appears in Fig. 181 where the dark nucleus in the upper group shows the granule of free

Fig. 181.—Microscopic test for free lime.

lime from which the plume-like crystals grow. No substance other than calcium oxide or hydroxide has been found to give this reaction.

Observations

Importance of the Test

The most important quality of cement is soundness, for no matter how high a degree of tensile strength a cement may develop at comparatively short periods, if it fails to resist the disintegrating influences of the atmosphere or the water in which it may be placed, it is useless as a material of construction. This tendency to disintegrate, fall to a powder, crack or expand on mixing the cement with water is termed "blowing." This fault

is usually due to improper proportioning of the raw materials, allowing an excess of lime over what will combine with the silica and alumina of the cement mixture; or an improper burning, failing to raise the temperature to the point where all the lime may combine with the silica and alumina, thus leaving some in the uncombined state; or from insufficient grinding of the raw materials for the lime to unite with the silica and alumina. This free or loosely combined lime on coming in contact with water is slacked and expands, causing the cement to crack and fall to pieces.

Causes of Unsoundness

Some discussion has been aroused of late as to what causes the failure of cement to stand the various tests for soundness. Some of the various compounds which may be present in cement, calcium disilicate, alkalies, etc., are said to promote checking in the boiling test. All authorities seem to agree, however, that the chief cause is the presence of free or unstable lime over and above a certain limit. This free lime slakes *after* the cement has itself hardened or set, causing the test piece to warp and check from the expansion set up by the change. The object of all tests for soundness is, therefore, to ascertain if the maximum of free lime that may safely be present has been exceeded.

A certain small percentage of free lime is present in all cement. I have frequently added as much as 5 per cent of unslaked lime (prepared from precipitated calcium oxalate, and hence very finely pulverized) to cement, and yet pats made from the mixture passed both boiling and twenty-eight-day tests. If the lime is coarser, the quantity which can be added is much smaller. Slaked lime may be added in large quantities without affecting either boiling or cold water pats; so may also carbonate of lime. Pats with any proportion of either are perfectly sound. Hydrated lime (mechanically slated lime) is now added to concrete extensively for water-proofing the latter. No fears need be experienced that such concrete will fail.

Effect of Seasoning on Soundness

Anything which promotes the changing over of the free lime into slaked lime or carbonate of lime will cause cement at first unsound to become sound. The air always contains the elements, moisture and carbon dioxide, to bring about such a change, so that if cement that is unsound is stored for any length of time it will gradually become sound, from the slaking and carbonating of the free lime. This is illustrated by the following table:

TABLE LX.—SHOWING EFFECT OF SEASONING ON SOUNDNESS.

Age in days after being ground[1]	Cement No. 1	Cement No. 2	Cement No. 3	Cement No. 4	Cement No. 5
	Results of 5-hour steam test (A. S. C. E.)				
0	Checked	Partly disintegrated	Checked	Checked	Entirely disintegrated
1	Checked	Badly checked	Checked	O. K.	Entirely disintegrated
3	Slightly checked	Badly checked	Slightly checked	.....	Partly disintegrated
7	O. K.	Checked	Slightly checked	.....	Badly checked
14	.....	Checked	O. K.	.....	Badly checked
21	.....	Slightly checked	.....	.....	Checked
28	.....	O. K.	..	.....	Checked
90	.....	.....	.....	.....	O. K.

[1] Samples were seasoned in a small paper bag on a shelf in the laboratory.

Cement which has seasoned sound is just as good as one which was sound when freshly made, and the writer does not think the engineer need concern himself whether the manufacturer prefers to make cement which is sound when fresh, or whether he prefers to age it sound in his stock-house. So long as it is sound when he uses it, he is secure, and possibly the softer burned

clinker, usually unsound when freshly ground, will grind with a greater percentage of flour, increasing the sand carrying capacity of the cement.

Effect of Fine Grinding of the Raw Materials on Soundness

In order for cement to stand the boiling test when fresh from the grinding mills, the raw materials must be finely ground. The unsoundness due to coarse grinding of the raw materials is prob-

TABLE LXI.—Showing Effect of Fineness of Grinding of Clinker on Soundness.

Condition of cement as tested	Fineness		Result of 5-hour steam test (A. S. C. E.)
	Residue No. 100	Residue No. 200	
As received from the mills, tested one day old	8.5	27.0	Partially disintegrated
As received from the mills, tested again after seasoning one week	8.5	27.0	Partially disintergated
As received from the mills, tested again after seasoning one month	8.5	27.0	Badly checked
Portion of sample passing No. 200 sieve, tested one day old	0.0	0.0	Sound
Sample ground to all pass a No. 200 sieve, tested one day old	0.0	0.0	Slightly checked
Sample ground to all pass a No. 200 sieve, tested one week after grinding	0.0	0.0	Sound

ably the hardest form of unsoundness to cure by aging. This is particularly so if the clinker has been burned very hard, as the coarse pieces of limestone, calcined to free lime, are locked up in a case of clinker. If this case is not broken in grinding, the free lime is left surrounded by a wall of clinker and will be very slowly acted upon by the moisture of the air. The experiment in Table LXI seems to prove this very thing. Laboratory records show the unsoundness of this sample to have been due to coarse grinding or the raw mixture. The fine particles passed the boiling test fresh, the coarse ones failed even on grinding, but on aging one week, the ground particles stood the test. Aging the

cement, however, for two weeks failed to make it sound, because the free lime was locked up in the coarse particles, where hydration could only take place very slowly, but, on grinding the coarse particles, the air had a chance to get at the free lime and convert it to the innocuous hydroxide.[1] The effect of fine grinding of the cement itself on soundness has been discussed in Chapter XXI.

Effect of Sulphates on Soundness

Pats allowed to harden in steam or hot water will often pass the boiling test where pats hardened in air will not. It must be remembered that checking is caused by slaking after the pats are fully hardened. If they are placed in steam to harden the moist air merely accelerates the slaking of the lime, doing the work before the pat hardens, just as heat hastens any chemical action. The addition of sulphates, either as gypsum or plaster of Paris, aids the cement in standing the boiling test, probably because it delays the set until after the lime has slaked. The rendering of the free lime inert by the formation of compounds with the lime by the gypsum seems hardly probable, since the lime and gypsum could not react unless both were in solution, and if the water could get at the free lime to dissolve it, slaking would take place on adding water only, and the harmless hydroxide would be formed. The early hardness due to gypsum can hardly play any part, since cements breaking as high as 600 pounds in twenty-four hours may fail on the boiling test, while briquettes breaking at 150 pounds may be sound. My own experiments go to show that anything which will delay the setting of cement until after the free lime has slaked, or that will hasten the slaking of the free lime before the pat sets, will make cement sound. The table given below shows the effect of additions of plaster on the boiling test:

[1] See also Taylor, *Proceedings, Am. Soc. Test. Mat.*, III (1903), 377, and Butler, Portland Cement, p. 174.

TABLE LXII.—Showing Effect of Additions of Gypsum or Plaster of Paris on Soundness.

Sample	Per cent SO_3	Result of 5-hour steam test (A. S. C. E.)[1]			
		0.5 per cent plaster added	1.0 per cent plaster added	2.0 per cent plaster added	3.0 per cent plaster added
Cement	1.21	Sound	.....	.....	.....
Cement	1.43	Checked	Sound	.....	.....
Cement	1.18	Checked	Checked	Sound	.....
Cement	1.36	Checked	Checked	Checked	Sound
Ground clinker	0.31	Checked	Checked	Sound	.....

[1] All samples were unsound without addition of plaster of Paris.

Value of Accelerated Tests

At the 1903 meeting of the American Society for Testing Materials, Mr. W. P. Taylor, of the Philadelphia Municipal Testing Laboratory, read a very carefully prepared paper upon the boiling test[2] in which he compared the results of neat briquettes and neat pats with the results of the boiling test. As is usual, he considered a falling off of the strength of neat briquettes on long time tests and a cracking and warping of the neat cold water pat as being positive evidence of the presence of injurious constituents in the cement. He gives these figures: "Of all the samples failing to pass the boiling test 34 per cent of them developed checking or curvature in the normal pats or a loss of strength in less than twenty-eight days. Of those samples that failed in the boiling test but remained sound for twenty-eight days, 3 per cent of the normal pats showed checking or abnormal curvature in two months, 7 per cent in three months, 10 per cent in four months, 26 per cent in six months, and 48 per cent in one year; and of these same samples 37 per cent showed a falling off in tensile strength in two months, 39 per cent in three months, 52 per cent in four months, 63 per cent in six months, and 71 per cent in one year. Or taking all these together, of all the samples that failed in the boiling test 86 per cent of them gave evidence in less than a year's time of possessing some injurious quality.

[2] *Proceedings, Amer. Soc. Test. Mat.*, III (1903), 374.

"On the other hand, of those cements passing the boiling test but one-half of 1 per cent gave signs of failure in the normal pat tests and but 13 per cent showed a falling off in strength in a year's time."

It is unfortunate that the test which seems to be accepted by the majority as a standard is the long time cold water pat, a test requiring such length of time for its completion as to practically forbid its use. The conditions of the case demand a rapid test in order that the consumer may not be required to store the cement for a long period of time while he awaits the results of his cold water pats.

Unquestionably much good concrete has been made from so-called unsound cement, and this is the key to the whole objection to the hot test. It is probable that much of the first American Portland cement would not have passed the steam test, yet it is upon the merits of the work done with this cement that engineers are now using American instead of imported cement. Butler gives a strong plea for the Faija test and states that in the twenty years this test has been in use, no cases of failure in work by cement passing this test have come under his observation. If the Faija test is severe enough to exclude all bad cements, then the steam tests is needlessly severe as it rejects many cements which pass Faija's test.

Some experiments[1] which were made by Mr. W. P. Gano, Chief Chemist of the Pennsylvania Cement Company, are interesting in this connection. He found by an extensive series of experiments that concrete would itself become sound, or in other words, that hydration could take place without necessarily causing destruction of the concrete. His experiments consisted in making a large number of test pats of each sample of unsound cement. One of these was subjected to the boiling test after twenty-four hours in moist air. The other pats were set aside in either air or water and subjected to the boiling test at intervals of a week or more. He found that the boiling test had less and less effect on the pats until eventually a period was reached when the pats stood the test perfectly. This would seem to indicate that

[1] *Engineering News*, Vol. LXVII, No. 21, p. 980.

those compounds causing unsoundness in the boiling test very frequently hydrate in a perfectly harmless manner and whatever expansion does occur will be taken care of by the elasticity of the concrete. In this connection, it should be remembered that as the concrete becomes older it becomes stronger and consequently better able to withstand any strains to which it may be put by expansives within itself.

All cement probably contains some free lime. From the nature of the case this must be so, since cement raw materials are not ground to a degree of fineness nor carried to a state of fusion which would permit of every molecule of lime coming in contact with a molecule of silica or of alumina. Now there are limits beyond which if the uncombined or free lime goes, certain results will take place. Let us suppose that with a very small percentage present the cement will fail on the boiling test but pass satisfactorily five hours in steam, and if a still larger percentage is present it will fail in the steam but pass the Faija test. Now, again, let us suppose that a neat mixture with a certain small percentage of free lime is sound, with a larger percentage a 3 : 1 sand mixture is sound, with a still larger percentage a 1 : 3 : 8 concrete is sound. (It is well understood that the tendency of cement to disintegrate is greater in a neat paste than in a sand mixture, and anyone with experience in cement testing knows of cases where neat briquettes had disintegrated in time and yet the sand ones were sound and strong). Now how do we know that the limit of lime which may be present in good cement (that is cement which will make enduring concrete) is coincident with that maximum which may be present for a sound boiling test?

Nearly all advocates of the steam test have tried to prove these two limits coincident by comparing the steam test with the results of neat pats and neat briquettes. Usually the coincidence of a failure on the boiling test with either a warping or cracking of the neat pats or a loss of strength in the neat briquettes on long time tests is considered competent evidence in favor of the boiling test. In reality cement is seldom used neat. A cement which fails on the boiling test, whose neat briquettes fall off in strength after seven or twenty-eight days, yet whose sand briquettes in-

crease in strength as they grow older, has certainly given evidence that it will make good concrete. In weighing evidence for any test it must be remembered that we do not make the soundness test to see if neat briquettes will fail in strength as they age or if neat pats will warp and decay, but whether sidewalks, piers, abutments, foundations, walls, floors and buildings of concrete, not neat cement, will be permanent, and the thing therefore to compare the boiling test with, is concrete. Not until we can compare our laboratory records with many examples of both failures and successes in actual work will we have reliable data for forming our conclusions as to the reliability of the various tests for soundness.

Experiments made by a committee of the Society of German Portland Cement Manufacturers in connection with the Royal Testing Laboratory at Charlottenburg forced them to report in 1900 and again in 1903 that none of the so-called accelerated tests for consistency of volume was adapted to furnish a reliable and quick judgment in all cases concerning the applicability of a cement. The experiments which they made consisted in putting the cement into actual work and observing it during a period of four years. The committee recommended the twenty-eight-day cold water pat as a standard test. If this test is taken as a standard the hot test will reject many good cements.

Manufacturing Conditions Influencing the Soundness

As has been previously pointed out, the manufacturing conditions which are most likely to cause unsoundness are those of too much lime in the cement, improper burning and too coarse raw material. In this connection, it should be remembered that there is a relation between these conditions as has been pointed out on pages 146 and 284.

The effect of lime on cement has been quite fully dealt with previously. The chemist who would have a satisfactory product can not, however, always cure unsoundness by resorting to the expedient of lowering the percentage of lime carried in the mix, because if he does this, he is likely to have a product which is quick-setting or of low strength, possibly both. Unsoundness

does frequently occur from too much lime where the fault is due to the inability of the chemist to have his raw mixture of the desired proportions. This is particularly true where unsoundness is caused by occasional excess of lime due to irregularity in the raw materials themselves.

There is a tendency on the part of manufacturers to go over to the wet process under the belief that it is easier to control the composition of the mix with this process than with the dry. In the matter of chemical control, there are unquestionably much better facilities provided at most wet process plants than there are in the general run of dry process mills. At the same time if proper facilities are provided, the dry process can be made to give fully as good results along this line as the wet process. The remedy for an irregular mix is usually the employment of a large stone store house or else silos such as are described on page 120, in which the raw material can be properly blended before being sent to the kilns.

Irregular burning is one cause of unsoundness. Generally speaking, all manufacturers aim to burn to about the same degree of hardness. Like many other manufacturing processes, however, the burning is dependent on the care with which it is done, or in other words, on the skill and attentiveness of the burners. The trouble is generally less a matter of the hardness to which it is aimed that the clinker be burned than of the fact that occasionally large amounts of underburned material are allowed to pass out of the kiln. The remedy in this case is obvious.

Coarse raw material probably causes more unsoundness than any other condition and generally speaking where plants are having continued trouble with the boiling test it is due to too coarse raw material. There has within the last ten years been a very marked change in the attitude of manufacturers in this respect, due very largely to the introduction of more efficient pulverizing machinery. There are now many plants where the raw materials are ground to a fineness of 85 per cent passing the No. 200 sieve.

While on the subject of fineness, it is well to point out that the ground raw material should be free from any considerable percentage of grit and it is well to test this through a 20-mesh sieve. There should be practically no residue on this sieve.

The general practice of seasoning clinker is an aid to soundness and a great deal of clinker which would not give sound cement if freshly ground will produce sound cement if seasoned for two or three weeks either in the open or where moisture can get to it. Mention has already been made of the practice of introducing steam into the tube mill, where these are used for grinding, and this practice is a material aid to soundness. There are objections to it, however, on the ground of inconvenience and possibly interfering with the efficiency of the tube mill itself.

Where the sulphur trioxide is not too near the limit, unsoundness may be often cured, as pointed out previously, by raising the percentage of this in the cement.

CHAPTER XXIV

TENSILE STRENGTH

Standard Specification and Method of Test

Specification.—7. The average tensile strength in pounds per square inch of not less than three standard mortar briquettes (see Sec. 50) composed of one part cement and three parts standard sand, by weight, shall be equal to or higher than the following:

Age at test, days	Storage of briquettes	Tensile strength, lbs. per sq. in.
7	1 day in moist air, 6 days in water	200
28	1 day in moist air, 27 days in water	300

8. The average tensile strength of standard mortar at twenty-eight days shall be higher than the strength at seven days.

Method of Operating Test

50. *Form of Test Piece.*—The form of test piece shown in Fig. 182 shall be used. The molds shall be made of non-corroding metal and have sufficient material in the sides to prevent spreading during molding. Gang molds when used shall be of the type shown in Fig. 183. Molds shall be wiped with an oily cloth before using.

51. *Standard Sand.*—The sand to be used shall be natural sand from Ottawa, Ill., screened to pass a No. 20 sieve and retained on a No. 30 sieve. This sand may be obtained from the Ottawa Silica Company, at a cost of three cents per pound, f. o. b. cars, Ottawa, Ill.

52. This sand, having passed the No. 20 sieve, shall be considered standard when not more than 5 grams passes the No. 30 sieve after one minute continuous sieving of a 500-gram sample.

53. The sieves shall conform to the following specifications:

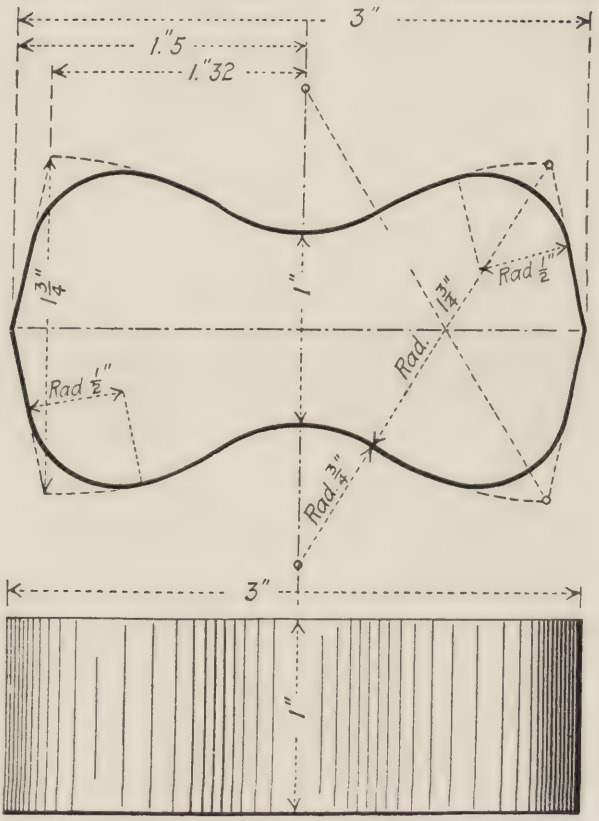


Fig. 182.—Details for Briquette.

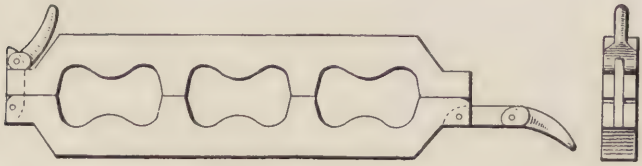


Fig. 183.—Gang mold.

TABLE LXIII.—PERCENTAGE OF WATER FOR STANDARD MORTARS.

Percentage of water for neat cement Paste of normal consistency	Percentage of water for one cement Three standard Ottawa sand	Percentage of water for neat cement Paste of normal consistency	Percentage of water for one cement Three standard Ottawa sand
15	9.0	23	10.3
16	9.2	24	10.5
17	9.3	25	10.7
18	9.5	26	10.8
19	9.7	27	11.0
20	9.8	28	11.2
21	10.0	29	11.3
22	10.2	30	11.5

The No. 20 sieve shall have between 19.5 and 20.5 wires per whole inch of the warp wires and between 19 and 21 wires per whole inch of the shoot wires. The diameter of the wire should be 0.0165 inch and the average diameter shall not be outside the limits of 0.0160 and 0.0170 inch.

The No. 30 sieve shall have between 29.5 and 30.5 wires per whole inch of the warp wires and between 28.5 and 31.5 wires per whole inch of the shoot wires. The diameter of the wire should be 0.0110 inch and the average diameter shall not be outside the limits 0.0105 to 0.0115 inch.

54 *Molding.*—Immediately after mixing, the standard mortar shall be placed in the molds, pressed in firmly with the thumbs and smoothed off with a trowel without ramming. Additional mortar shall be heaped above the mold and smoothed off with a trowel; the trowel shall be drawn over the mold in such a manner as to exert a moderate pressure on the material. The mold shall then be turned over and the operation of heaping, thumbing and smoothing off repeated.

55. *Testing.*—Tests shall be made with any standard machine. The briquettes shall be tested as soon as they are removed from the water. The bearing surfaces of the clips and briquettes shall be free from grains of sand or dirt. The briquettes shall be carefully centered and the load applied continuously at the rate of 600 pounds per minute.

56. Testing machines should be frequently calibrated in order to determine their accuracy.

57. *Faulty Briquettes.*—Briquettes that are manifestly faulty, or that give strengths differing more than 15 per cent from the average value of all test pieces made from the same sample and broken at the same period, shall not be considered in determining the tensile strength.

Storage of Test Pieces

58. *Apparatus.*—The moist closet may consist of a soapstone, slate or concrete box, or a wooden box lined with metal. If a wooden box is used, the interior should be covered with felt or broad wicking kept wet. The bottom of the moist closet should be covered with water. The interior of the closet should be provided with non-absorbent shelves on which to place the test pieces, the shelves being so arranged that they may be withdrawn readily.

59. *Methods.*—Unless otherwise specified, all test pieces, immediately after molding, shall be placed in the moist closet for from twenty to twenty-four hours.

60. The briquettes shall be kept in molds on glass plates in the moist closet for at least twenty hours. After from twenty to twenty-four hours in moist air the briquettes shall be immersed in clean water in storage tanks of non-corroding material.

61. The air and water shall be maintained as nearly as practicable at a temperature of 21° C. (70° F.).

Notes

Standard Sand

Up to the adoption of the above standard rules, crushed quartz such as is used in the manufacture of sandpaper, and of the same size as is specified for the present standard sand, was used, having been recommended by a former committee of the American Society of Civil Engineers.

Where the value of the cement is desired with regard to some particular piece of work, the sand used for the test may be the sand that is to be used for the work. In this case it is the mortar that is tested rather than the cement. Just as a series of tests

made with a standard sand and various brands of cement would give the comparative value of the cements, so a series of tests with an established brand of cement and various sands will give the comparative value of the sands.

Cement, when tested with the natural Ottawa sand, usually shows a greater strength than when tested with crushed quartz. In the case of seven-day breaks, the higher figure may be as much as 40 per cent above the lower. The reason[1] for this difference is due to the shape of the sand grains. The Ottawa sand being round, it compacts much more closely and has a lower percentage of voids than crushed quartz, as the latter has sharp and angular grains, which mass and wedge, leaving more space between the sand particles.

Other Forms of Briquettes

Fig. 184 shows the form of briquette recommended in the report of a former committee on a uniform system for tests of cement of the American Society of Civil Engineers,[1] which is similar to the present standard except that the latter has rounded

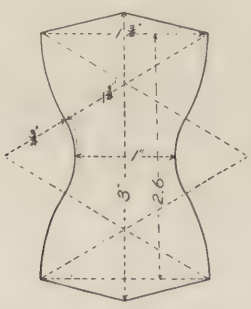


Fig. 184.—Old standard form of briquette.

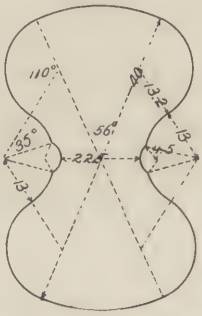


Fig. 185.—German standard form of briquette.

corners. Fig. 185 shows the form which is the standard in Germany. The dimensions of the two forms are given in the drawings. As will be seen, the weakest section of briquettes of either form is at the center and is one inch in cross-section,

[1] Brown, *Proceedings of Am. Soc. for Test. Mat.*, IV (1904), 124.

[1] This committee presented its report at the annual meeting of the society, January 21, 1885, and was then discharged.

in the case of the United States standard; and 5 square centimeters in that of the German. Comparative tests show the American standard to give the higher result of the two. In the case of briquettes of neat cement, this difference amounts sometimes to as much as 30 or 40 per cent of the lower. The standard British form of briquette is the same as the A. S. T. M. form.

Molds

Other types of briquette molds are shown in Fig. 186. The first form is held together by levers, the bearing surfaces of which are the ends of threaded pins. By turning the pins as they wear, the molds can be kept tightly closed. The second form is held together by a clamp provided with a thumb screw but in the writer's opinion has no advantage over the standard form and the disadvantage of an extra part—in the case of a gang mold two extra parts. The third form is provided with an eccentric bearing so that when it is revolved in a half circle, or over, to the

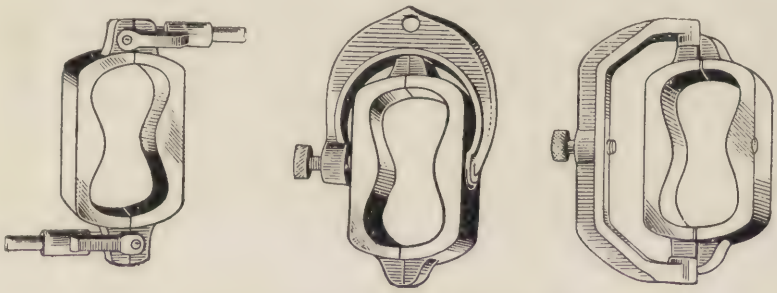


Fig. 186.—Other forms of briquette molds.

other side from that shown, the two halves of the mold are separated, thus facilitating the removal of the briquettes. All these types are adapted to three-gang molds.

Fig. 187 shows form of gang mold which is extensively used. Where molds are for more than three briquettes it is advisable to bore a hole through from side to side of the mold, between the second and third openings, so as not to interfere with the briquettes, and to run a bolt provided with a thumb-screw

through this. The mold will be considerably stiffened thereby and springing will be guarded against.

Molds are usually made of gun-metal, brass, bronze or some alloy of copper which does not rust on exposure to moisture. Mr. Force, Engineer of Tests of the Lackawanna R. R., tried

Fig. 187.—Good form of gang mold.

aluminum molds but found that while they were light and stiff enough, the test-pieces stuck to them badly.

To clean the molds, lay them all flat on the table without the clamps just as if briquettes were to be made and scrape off any hardened cement with a piece of sheet zinc or other soft metal. Then brush off with a stiff bristle brush and wipe with a piece of oily waste. Turn the molds over and repeat the process on the other face. Now separate the molds and place the halves in a long line with the mold part forming a trough, brush with

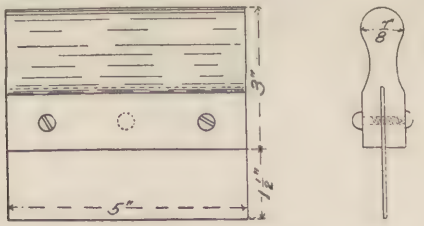


Fig. 188.—Scraper for cleaning molds.

a stiff brush and wipe off with oily waste. Briquettes should not be allowed to become too hard before removing from the molds. The specifications require that the briquettes be left in the molds for at least twenty hours and this is long enough if the cement is normal.

Fig. 188 shows a scraper for cleaning molds. This consists of a block of wood 5 × 3 inches, rounded to form a handle, into which is fixed a piece of zinc.

Mixing

In place of a glass plate, a sheet of brass ⅛-inch thick makes an excellent mixing surface. Slate and soapstone slabs are also used. Both, however, absorb water and draw it away from the briquettes. This can be avoided by keeping a damp cloth over that part of the table used for mixing when not in service. Or

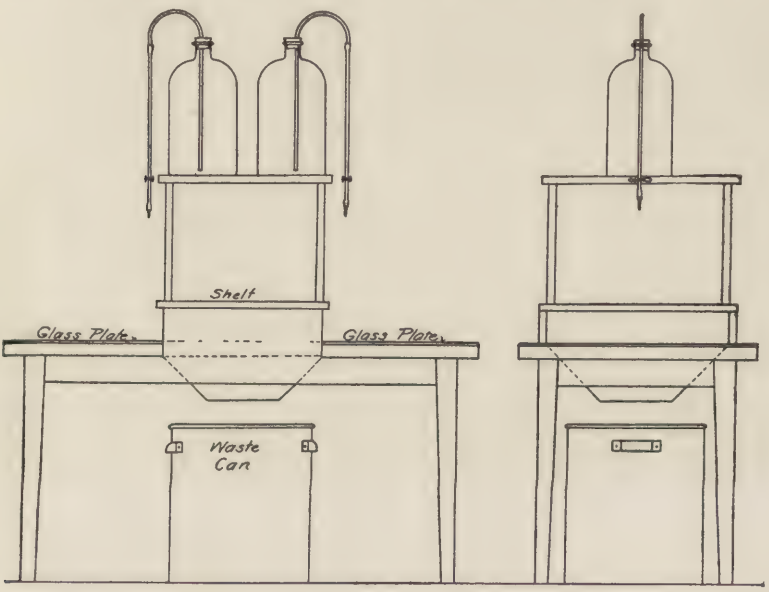


Fig. 189.—Table for mixing mortar and making briquettes and pats.

melted paraffine may be poured over the heated slab and allowed to soak in and the whole then cooled. The excess of paraffine is, of course, to be scraped off with a metal scraper.

Fig. 189 shows a convenient table for mixing mortar and making briquettes and pats. It consists of a table arranged with glass or brass plates or slate slabs at either end and the central

part of the table raised four or five inches above the ends as shown. The space between the shelf and the glass plate is left open so that the surplus mortar, etc., used in making a set of briquettes may be swept through this and into a waste can placed below. A piece of tin bent to form a trough, as shown, conducts the waste into the can. Above the first shelf, which is used for the scales, measuring cylinders, pat glasses, etc., a second shelf is supported by four uprights—one at each corner. At each end of this shelf are to be placed 2 gallon bottles provided with siphons of glass and rubber as shown. These siphons are closed by pinch-cocks, as shown. Drawers may be placed in front of the table for holding such articles as trowels, spatulas, etc. Four 2-gallon bottles should be provided, and while two are in use on the table the other two should be full and standing nearby to get the room temperature.

Instead of kneading the cement mortar with the hands as prescribed by the standard rules, many testers use a trowel, working the mortar back and forth on the table, under the trowel.

Percentage of Water

The percentage of water used in gauging the mortar for the test pieces has a considerable influence on the strength of the cement. This is shown by the table given below which is taken

TABLE LXIV.—Influence of Various Proportions of Water on the Neat Strength of Portland Cement. (E. S. Larned).

Cement brand	Water per cent	Tensile strength 24 hours	7 days	28 days	3 months	6 months	12 months
	15	371	655	875	941	720	787
	16	303	750	973	1008	735	816
Giant	18	260	649	773	831	645	748
Portland	20	233	500	693	716	621	676
	22	184	546	636	658	601	589
	24	167	539	649	644	629	755
	13	366	775	859	1067	892	832
	14	404	780	891	972	852	781
Atlas	16	363	602	725	844	806	723
Portland	18	308	570	723	785	728	724
	20	225	590	718	760	674	636
	22	116	554	649	731	643	604
	24	42	510	691	695	632	574

from a paper by Mr. E. S. Larned[1] on the subject. It will be noticed that in the case of both cements, the dryer mixtures give the higher results. This is probably due to the fact that the dry mixtures require hammering or ramming to get them in the molds, while the wet mixtures were merely forced in with the thumb as they were too soft for this treatment. Other experimenters, however, have found results differing in some particulars from Mr. Larned, and while agreeing with him that the dryer mixtures give higher short time tests, their experiments show the differences on long time tests to be slight and usually in favor of the wet mixtures. This has also been the writer's experience, but in his case both the dry and the wet mixtures were merely pressed into the molds with the thumbs.

Table LXIII gives the percentage of water to be used in standard mortars. This table is calculated from the formula:

$$Y = \frac{0.67P}{N+1} + K.$$

In which Y is the percentage of water required for sand mortar, P is the percentage of water required for neat cement paste of normal consistency, N is the number of parts of sand to one of cement by weight and K is a constant which for standard Ottawa sand has the value 6.5.

This table differs quite materially from the one formerly used. The former methods (Am. Soc. Civil Engrs.) called for a much dryer mortar as the following Table LXV will show.

TABLE LXV.—Comparison between Old and New Specifications for Percentage of Water for Standard Mortars.

Percentage of water for neat cement Paste of normal consistency	Percentage of water for one part cement to three of standard Ottawa sand by weight	
	Old specifications	Present specifications
18	8.5	9.5
19	8.7	9.7
20	8.8	9.8
21	9.0	10.0
22	9.2	10.2
23	9.3	10.3
24	9.5	10.5
25	9.6	10.7
26	9.8	10.8
27	10.0	11.0
28	10.2	11.2

[1] *Proceedings, Amer. Soc. Test. Mat.*, III (1903), 401.

The old figure is based on a value for K of 5.5. Feret who originally devised this formula in a somewhat different form used a value for K of 6.0 for mortars of plastic consistency and 4.5 for mortars of dry consistency.

Storage of Briquettes

The briquettes may be placed in water either flat or on edge. The latter gives more surface exposed to the water. The tanks in which the briquettes are immersed may be made of galvanized iron and of any desired size. They are usually, however, from 2 to 6 inches deep. Where space is limited, they may be placed one above the other on a suitable framework.

When much testing has to be done, a good form of trough for the storage of briquettes is made of stout 2-inch board lined with sheet zinc. These troughs may be placed one above the other on a suitable wood frame. A small stream of water should be kept running through them all the time. This can be done by arranging overflow tubes so that the water will flow from the upper trough into the next one below, etc.

Quite frequently the briquette trough is placed in the cellar

Fig. 190.—Marking briquettes.

and is made of concrete. In one of the writer's laboratoriess such a trough is employed. It is raised about 2 feet from the floor and is 8 inches deep. The water level is maintained at about 6 inches. The temperature of this cellar is very even

both in summer and winter. In making the trough, a very dense concrete was used so as to be sure of no leakage from it into the cellar.

After the briquettes have attained their initial set they should be marked with an identifying number. Where neat briquettes are made these may be marked by a steel die as shown in Fig. 190. Sand briquettes may be marked by putting a thin layer of neat cement about 1/16 inch thick on one end and marking this. When briquettes are to be broken at short periods a grease pencil such as is used for marking china may be used for marking, but where long time tests are made steel dies should be used.

In storing the briquettes in the troughs, it will be found most convenient to put all the briquettes to be broken in seven days, in order of making, in one part of the trough, and those for twenty-eight days in another, etc. The briquettes may be placed edgewise, in pairs, one on top of the other; and where the sand briquettes are not marked, it will be found a good plan to place the neat briquettes over the corresponding sand ones.

The number of briquettes to be made, and the time when these are to be broken, will vary with circumstances. Usually in cement inspection work only seven-day and twenty-eight-day sand tests are made but in research work briquettes are often made to be broken at periods of twenty-four hours, seven days, twenty-eight days, three months, six months, one year, two years, five years and ten years. Uusually from three to five briquettes, both sand and neat, are broken at each period, except at twenty-four hours, when only neat briquettes are broken. In temporary and field laboratories the long time tests are, of course, omitted. Three briquettes are usually considered enough to test the strength of cement at any period, though in some laboratories only two of each kind are broken.

The briquettes should always be put in the testing machine and broken *immediately* after being taken out of the water, and the temperature of the briquette and of the testing room should be constant, between 60° and 70° F. Seven days neat briquettes kept in the room and allowed to dry out for twenty-four hours

before breaking, in many instances, break at less than half the strain of those kept in water the full period. Sand briquettes, however, seldom show any very marked difference.

Testing Machines

The Fairbanks[1] cement testing machine is much used for cement testing because of its simplicity and automatic action. It is shown in Fig. 191. It consists of a cast iron frame A, made in one piece with a shot hopper B. To this frame are hung the

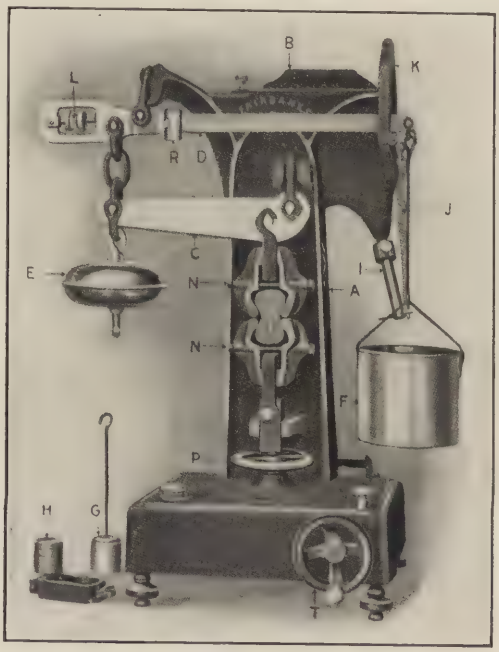


Fig. 191.—Fairbanks cement testing machine.

two levers D and C. From the end of the upper lever the weight is applied by allowing shot to flow from the hopper into the bucket F. The tension is applied to the briquette held in the

[1] The Fairbanks Scale Co., New York, N. Y.

clips N and N by means of the lower lever C. The lower clip is attached, by means of a ball joint, to a screw with a hand wheel P, for lowering or raising, when putting in the briquette and taking up the slack. There is also a counterbalance E, for bringing the levers and bucket into partial equilibrium so that the final adjustment can be made with the ball L. The shot hopper is provided with a lever and gate J, which cuts off the shot as soon as the specimen breaks. The shot is weighed by hanging the bucket on the opposite end of the lever D, by means of a sliding poise R.

To operate the machine:

Hang the cup F on the end of the beam D as shown in the illustration. See that the poise R is at the zero mark, and balance the beam by turning the ball L.

Fill the hopper B with fine shot, place the specimen in the clamps N N, and adjust the hand wheel P so that the graduated beam D will rise to the stop K. Open the automatic valve J so as to allow the shot to run slowly into cup F. When the specimen breaks, the graduated beam D will drop and automatically close the valve J.

As the load is applied, the beam D will begin to drop. When it reaches a point midway in the guide K, jointly engage the hand wheel T and turn slowly so as to keep the beam D from striking the bottom of the guide and cutting off the flow of shot before the briquette breaks.

Remove the cup with the shot in it, and hang the counterpoise weight G in its place.

Hang the cup F on the hook under the large ball E, and proceed to weigh the shot in the regular way, using the poise R on the graduated beam D, and the weights H on the counterpoise weight G.

The result will show the number of pounds required to break the specimen.

The flow of shot can be regulated by the valve, M.

Many operators prefer to operate this machine by applying sufficient force at the start to take care of the elasticity of the cement and by so doing no attention is needed while the briquette

is breaking unless the beam falls to the bottom of the guide when the flow of shot will be cut off. This method of procedure is convenient but is likely to result in premature breaks, particularly if the operator is inexperienced or the cement is weak.

In the Fairbanks machine there is an error due to the fact that some time (in which shot is falling into the bucket) is taken by the beam to fall to the valve checking the shot stream; this

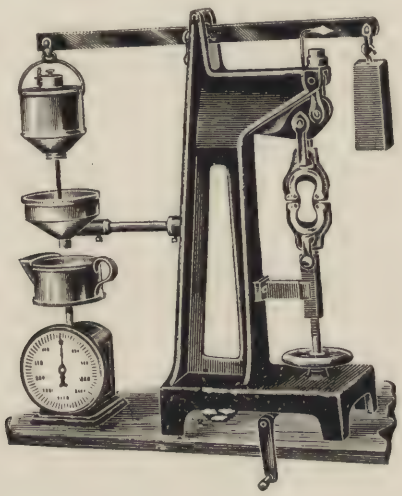


Fig. 192.—Riehlé U. S. standard automatic cement tester.

stream of shot extending from the valve opening to the surface of the shot in the bucket must fall into the latter and be weighed as part of the load which broke the specimen, though this shot was not in the bucket when the specimen broke.

Fig. 192 shows the Riehlé automatic testing machine.[1]

In this machine the initial load is avoided by an ingenious arrangement consisting in balancing a bucket of shot against a weight, and then applying the load by allowing the shot to run out of the bucket.

This load acting through the levers breaks the briquette. The beam should be kept horizontal by means of the lever and worm

[1] Riehlé Bros. Testing Machine Co., Philadelphia, Pa.

gear so that the pointer and mark on the beam are at all times practically coincident.

At the instant that the test piece breaks, the flow of shot is shut off by means of a piston valve. The shot flowing out of the kettle is caught in a large cup resting on a spring balance, which shows at all times the load which has been applied to the briquette. As soon, therefore, as this latter breaks, the operator can see at a glance the strain required to do this.

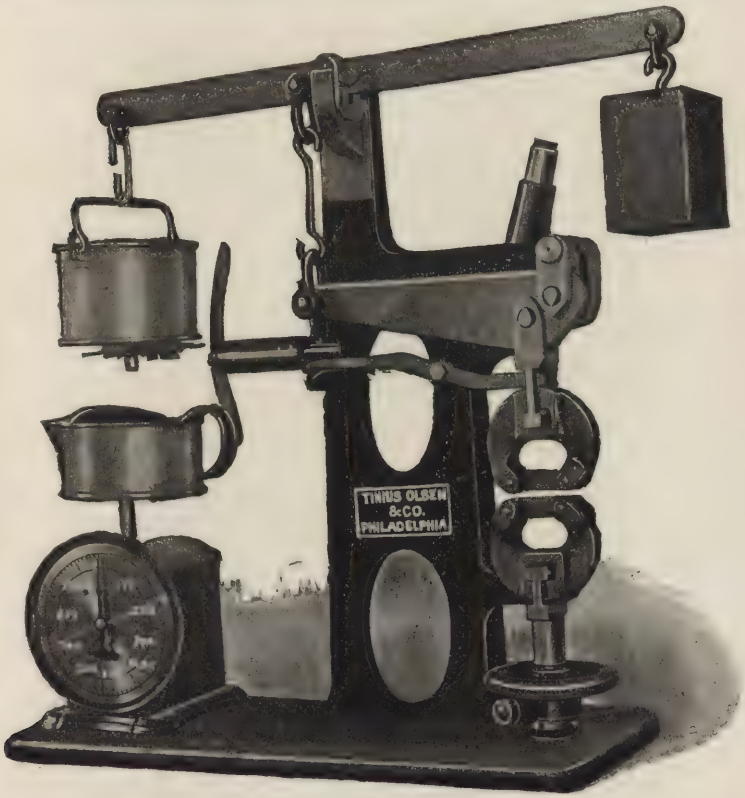


Fig. 193.—Olsen shot machine.

These machines have come into very extensive use of late years, as they have many points of advantage over the older forms. For instance there is no initial load applied. The break-

ing stress is read directly as soon as the briquette breaks and there is no transferring of the shot from one end of the beam to the other in order to weigh it. The weight and impact of the flowing column of shot is also done away with.

The Olsen shot machine[1] is shown in Fig. 193. It is somewhat similar to the Riehlé machine, although in the author's opinion the latter possesses some points of advantage over the former. In this machine the valve is different from that of the Riehlé.

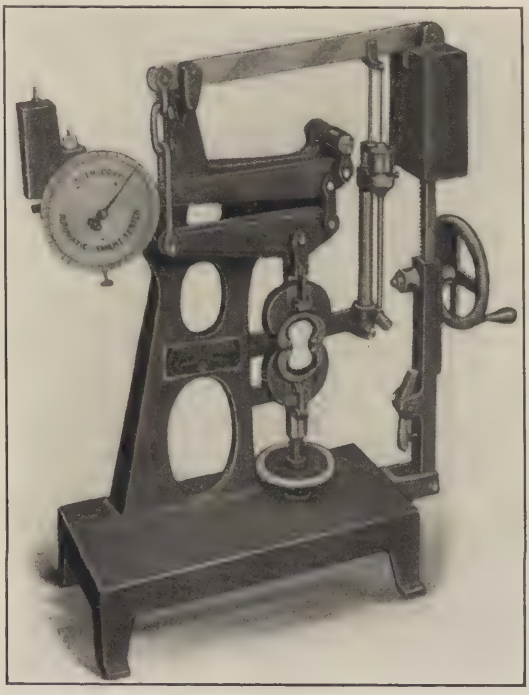


Fig. 194.—Olsen-Boyd automatic cement tester.

In the Olsen machine the briquette is placed in the clips and the load applied by means of the small hand wheel located below these. This small wheel is so arranged that it will automatically slip on the adjusting screw as soon as the predetermined initial

[1] Tinius Olsen Co., Philadelphia, Pa.

load has been applied to the briquette. The cut-off of shot is effected by the upper grip striking the horizontal arm which extends just above it, and thus releasing the curved arm carried on the spindle immediately on the left. This curved arm in turn strikes the valve and closes it.

The newest type of cement tester to be brought out is the Olsen-Boyd machine (Fig. 194). This is also made by Tinius Olsen Testing Machine Company, Philadelphia. This machine has all the advantages of the shot type of machine but does not employ any shot. This is desirable since the shot have to be returned to the kettle after each test and during this transfer are apt to be spilled.

In this machine the initial load is applied as with the shot type of machine by means of the lower hand wheel. A ratchet arrangement at the base can be set so as to cut off the pressure here at any desired initial load even though the operator continues to turn the hand wheel. This guards premature breaks. The breaking load is applied by means of the weight at the right of the machine which moves downwards, the motion being controlled hydraulically so as to give a uniform rate of loading of 600 pounds per minute or any other rate desired. The load is indicated continuously as applied by means of the pointer and dial, the former remaining at the maximum point of load when the briquette breaks. After the briquette is broken and is removed from the clips, the pointer is set at zero by pushing up the plunger shown below the dial and the weight to the right is raised to the initial point by the hand wheel when it is automatically latched in place. These operations can be quickly done, when the machine is ready for another test. In spite of the short time in which this machine has been on the market it is extensively used.

Rate of Stress

Whatever machine is employed to break the briquettes the load is to be applied at the rate of 600 pounds per minute. The standard load for many years was 400 pounds per minute but the committee of the American Society of Civil Engineers in their

report of 1903 increased this to the above figure. The more rapidly the load is applied to a cement briquette, the higher the breaking figure which will be obtained. Any of the automatic shot testing machines described above can be set so that the load will be applied at a uniform rate.

Clips

Some of the various forms of clips are shown in the following illustrations. Fig. 195 shows that recommended by the former

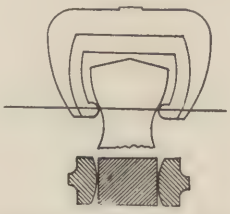


Fig. 195.—Old standard clip.

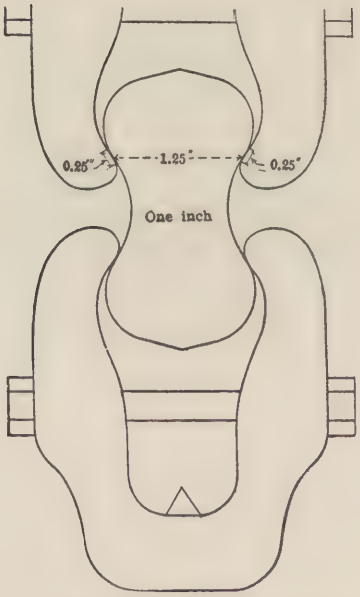


Fig. 196.—Standard form of clip.

committee of the American Society of Civil Engineers. This form does not seem to be very satisfactory as the bearing surface is insufficient and the briquette is likely to break from the crushing of its surface at the point of contact. A later form of clip Fig. 196 is much more to be preferred. It affords sufficient bearing surface without binding.

Various authorities at different times have advocated cushioning the grips by placing blotting paper between the jaw of the grip and the briquette, or stretching rubber bands around the

Fig. 197.—Rubber cushioned clip.

jaws, so as to soften the point of contact of these with the test piece. Mr. W. R. Cock[1] advised the use of a rubber bearing as shown in Fig. 197. In this clip the line of contact between the grip and the briquette is a rubber tube mounted on a

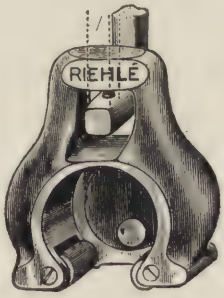


Fig. 198.—Roller clips.

pin. These tubes are readily replaced for a few cents when worn out. These cushion clips usually give results which are only 80 to 90 per cent of those obtained with the standard clips. The cushion clips are also troublesome.

[1] *Engineering News*, Dec. 20, 1890.

Roller clips (Fig. 198) are now as stated much used. Roller bearings are likely to wear flat unless they are kept clean and can revolve freely. This it is hard to do. Roller clips do not give breaks that are any higher than those obtained with the Standard rigid form. The general impression seems to be that clip breaks are due to cross strains and hence give figures below the true breaking strength of the cement. In fact, experiments prove that clip breaks are on an average from 2 to 5 per cent higher than breaks obtained at the cross-section.

The roller clip shown in Fig. 198 has a solid back which prevents the briquette from being shoved too far back in the clip. This or some form of stop is desirable with any form of clip.

In order that the stress upon the briquette shall be along the proper lines great care must be exercised in properly centering the briquette in the clips, and the form of the latter must be such that it does not clamp the head of the briquette thus preventing the test piece from adjusting itself to an even bearing. At the same time the surface of contact must be sufficient to prevent the briquette from being crushed at this point. Striking the happy medium has so far proved not any too easy. The clips are usually suspended by conical bearings which permit them to turn so as always to transmit the stress in a direct line between the bearings.

Other Methods

Foreign Specifications

The British test briquette is of the same form and dimensions as our own. Their sand is a natural sand also, but the British specifications call for both neat and sand tests. The molds are filled by hand with a special form of spatula. The requirements call for a minimum neat strength at seven days of at least 450 pounds and a 1:3 sand strength of 200 pounds. The twenty-eight-day neat test must not be less than 500 pounds and the increase in strength from seven to twenty-eight days must not be less than

25 per cent if the 7 day test is between 400 and 450 lbs.
20 per cent if the 7 day test is between 450 and 500 lbs.
15 per cent if the 7 day test is between 500 and 550 lbs.
10 per cent if the 7 day test is between 550 and 600 lbs.
5 per cent if the 7 day test is over 600 lbs.

The sand strength at twenty-eight days must not be less than 250 pounds and the increase in strength from seven to twenty-eight days must not be less than

25 per cent if the 7 day test is between 200 and 250 lbs.
15 per cent if the 7 day test is between 250 and 300 lbs.
10 per cent if the 7 day test is between 300 and 350 lbs.
5 per cent if the 7 day test is over 350 lbs.

The standard German specifications, like our own, call for no neat test. The form of briquette has been shown in Fig. 185. The Steinbrüch mixer and the Bohmé hammer are employed for mixing the mortar and tamping the molds respectively. The specifications call for a sand strength of at least 12 kilograms per square centimeter which is equivalent to 171 pounds per square inch. The specifications require no twenty-eight day tensile strength test but do require a seven and twenty-eight-day compressive 1:3 sand test equivalent to 1,708 pounds and 2,846 pounds per square inch minimum respectively for the two periods.

The standard French specifications call for both neat and sand tests. The form of briquette is the same as that shown in Fig. 185. The mortar is hand mixed and the molds hand filled. The requirements are:

	Kilos per sq. cm.	Lbs. per sq. in.
7 days neat	25	356
28 days neat	35	498
Increase between 7 and 28 days neat	3	42.7
7 days 1:3 sand	8	114
28 days 1:3 sand	15	213
Increase between 7 and 28 days sand	2	28.4

The above specifications are the minimum and the engineer can increase them if he should so desire.

Lack of Uniformity in Tensile Tests

In cement testing, the personal equation enters very largely into the results. In a paper[1] by Prof. James Madison Porter, of

[1] *Engineering News*, March 7, 1895.

Lafayette College, he gave a series of results upon the same cement by nine different operators, tested by the method of the Society of Civil Engineers as they understood it. The results varied from 75 to 247 pounds per square inch. The first Committee on a Uniform System for Tests of Cement of the American Society of Civil Engineers, in their report, says:

"The testing of cement is not so simple a process as it is thought to be. No small degree of experience is necessary before one can manipulate the materials so as to obtain even approximately accurate results.

"The first test of inexperienced, though intelligent and careful persons, are usually very contradictory and inaccurate, and no amount of experience can eliminate the variations introduced by the personal equations of the most conscientious observers. Many things, apparently of minor importance, exert such a marked influence upon the results, that it is only by the greatest care in every particular, aided by experience and intelligence that trustworthy tests can be made."

The personal equation probably plays its most important part in the gauging of the cement, the making of the mortar, and the molding and breaking of the briquettes. In order to eradicate these variations of treatment, machines have been introduced upon the market to do the work automatically and so do away with whatever variations the operator may introduce into the hand work, principally among which are the *Steinbrüch* and the *Faija mixers* and the *Bohmé hammer*. None of these machines, however, give test pieces which are more uniform than hand made ones.

Machines for Mixing the Mortar and Making Briquettes

The *Steinbrüch* mixer is much used in Germany. It consists of a horizontal circular casting having on its upper side near the outer edge a groove or trough in which a wheel whose rim corresponds with the groove of the pan rests. Both the pan and the wheel revolve and the mortar is rubbed between the surfaces of the wheel and the trough. Ploughs keep the mortar in the center of the trough.

The *Faija* mixer is the design of the late Henry Faija, of England and is listed in the catalogue of Riehlé Bros. Testing Machine Company, of Philadelphia.

The *Taylor* mixer is the design of Mr. W. P. Taylor and was used by him while in charge of the Municipal Cement Testing Laboratory of Philadelphia. It is listed in the catalogue of Tinius Olsen Testing Machine Company, Philadelphia.

The *Bohme* hammer[1] consists of a tilt hammer with automatic action, which hammers the cement mortar into the mold. It is listed by both of the firms mentioned above. The Olsen molding machine fills the mold by compression applied by a hand wheel through a plunger. It is made by Tinius Olsen Testing Machine Company. None of these machines have been used to any extent for testing cement in this country. Those who are interested in machines for mixing the mortar and molding the briquettes are referred to the earlier editions of this book or to the standard English and German works on cement testing.

Observations

High Tensile Strength of Unsound Cement

Much attention was formerly paid to neat strength but as the result of the opposition of the writer and other cement experts to this practice, the neat test has now been dropped from the standard specifications. Unsound cements often give notoriously high results, and the addition of plaster or gypsum will also increase the neat strength. In both of these instances there is apt to be on long time breaks a falling off in strength, permanent in the former case and usually only temporary in the latter case.

This is illustrated by the following table taken from a paper by Mr. W. P. Taylor, on "Soundness Tests of Portland Cement,"[1]

TABLE LXVI.—Comparison of the Tensile Strength of Briquettes Passing and Failing in the Boiling Test.

Age	Failing		Passing	
	Neat	1 : 3 sand	Neat	1 : 3 sand
1 day	530	...	391	...
7 days	817	197	643	237
28 days	749	273	727	303
2 months	713	274	732	312
3 months	702	242	749	314

[1] *Trans., Am. Soc. C. E.*, 3, p. 1.

[1] *Proceedings, Amer. Soc. Test. Met.*, III (1903), 381.

read in 1903. This table was compiled from over 200 nearly consecutive tests of a single brand, 100 of them failing in the test, 100 passing.

It will be noticed that the early strength of the neat tests of those samples failing to pass the test is much the greater, while the opposite is true of the sand samples.

Relation Between Neat and Sand Strength

That the sand strength and neat tests do not necessarily bear any relation to each other, the Table LXVII will show. The

TABLE LXVII.—SHOWING LACK OF ANY RELATION BETWEEN NEAT AND SAND STRENGTH.

Cement No.	Boiling test	Fineness		Tensile strength 7 days		Tensile strength 28 days	
		Through No. 100	Through No. 200	Neat	1 : 3	Neat	1 : 3
1	O. K.	99.0	80.0	915	303	1013	353
2	O. K.	99.0	80.0	790	285	853	320
3	O. K.	99.1	85.1	933	298	990	340
4	O. K.	98.8	83.3	930	288	963	330
5	O. K.	94.8	78.8	733	270	825	360
6	O. K.	95.0	79.0	748	280	620	275
7	O. K.	96.5	74.0	818	273	858	360
8	O. K.	97.0	74.0	800	260	1013	280
9	O. K.	95.1	70.0	910	190	1038	266
10	O. K.	95.0	70.0	683	180	750	320
11	O. K.	98.0	82.5	1008	200	1115	282
12	O. K.	97.9	82.5	855	283	970	333
13	O. K.	94.8	75.0	610	350	810	440
14	O. K.	92.0	70.0	544	206	884	261
15	O. K.	93.4	70.4	701	217	893	310
16	O. K.	93.8	74.2	680	359	791	410
17	O. K.	97.1	82.5	855	283	970	333
18	O. K.	97.4	82.7	910	255	970	305

sand strength seems to depend largely upon the fineness, yet different brands of cement giving similar residues on the test sieves will not necessarily show the same relation between neat and sand test. This latter may, of course, be due to differences in the amount of flour, which is not shown by the sieve test, as well as to peculiarities of composition, physical structure, etc., of the clinker from which the cement is ground.

The opinion is also becoming more and more general that there is little relation between the tensile strength of sand bri-

quettes and of concrete. This is illustrated by the tests given in Table LXVIII. Each cement in this is a sample of a different brand and the four represent cement made in different sections of the country and from several kinds of material. From this and from numerous other tests which have been made it would appear that while the sand test is of value in determining whether cement is fit for use or not, it should not be used as a basis for comparatively valueing cements. It will also be seen that the tests are much nearer together at twenty-eight days than at seven days, and also that the difference between the compressive strength of the four cements at twenty-eight days is slight, the lowest figure being only about 10 per cent less than the highest.

TABLE LXVIII.—Comparison between Tensile Strength of 1:3 Sand Mortar and Compressive Strength of Concrete.

Cement	Setting time		Fineness	Tensile strength 1 : 3 sand		Compressive strength 1 : 2 : 3 concrete	
	In'l. min.	Fin'l. min.	No. 200 %	7 days lbs.	28 days lbs.	7 days lbs.	28 days lbs.
A	210	380	80.1	235	382	1805	2403
B	200	355	80.0	280	342	1370	2280
C	225	400	76.1	249	390	957	2161
D	165	360	83.5	246	290	1625	2328

Cements Arranged in Order of Strength.

Tensile strength 1 : 3 sand				Compressive strength 1 : 2 : 4 concrete			
7 days		28 days		7 days		28 days	
Cement	% of highest	Cement	% of highest	Cement	% of highest	Cement	% of highest
B	100	C	100	A	100	A	100
C	89	D	100	D	90	D	97
D	88	A	98	B	76	B	95
A	84	B	88	C	53	C	90

Effect of Seasoning and Hydration on Strength

The Structural Materials Research Laboratory[1] has made an extensive investigation of the effects of storage on the strength of concrete. This covered a period of five years and three different lots of Portland cement, the cement being stored under cover in standard cotton sacks. As the result of this investigation it was found that there is an appreciable loss in the strength of Portland cement due to storage and that the loss of strength

[1] *Bul. No. 6,* Structural Materials Laboratory, Lewis Inst., Chicago.

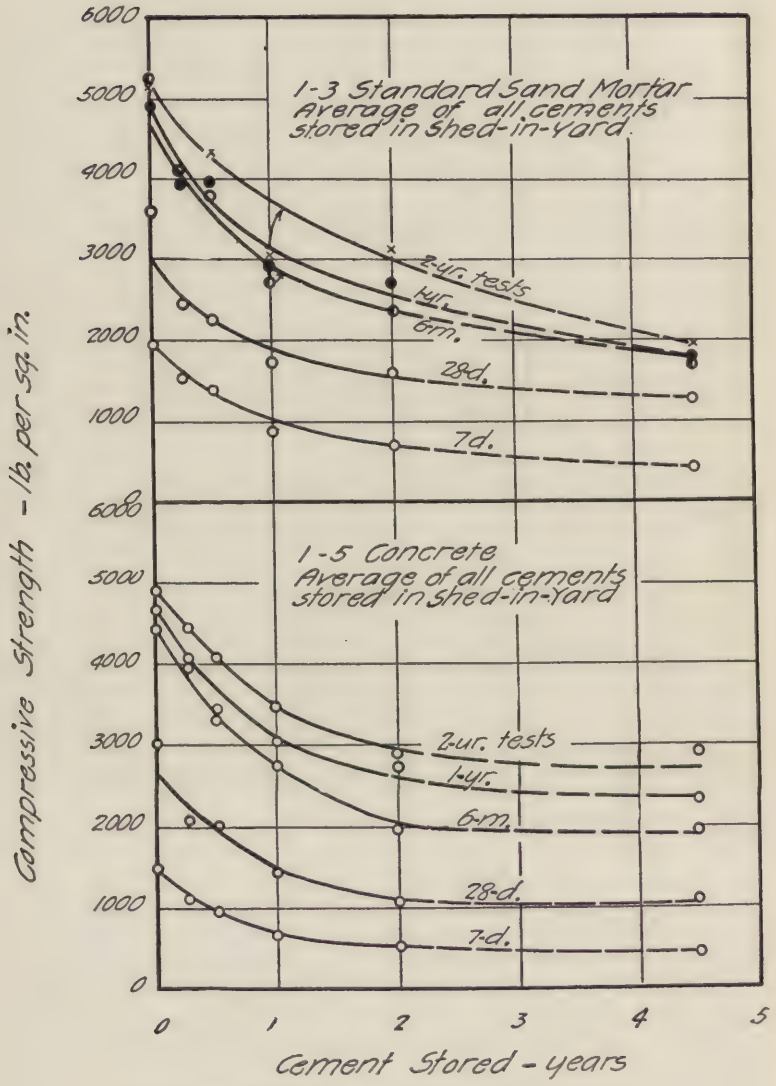


Fig. 199.—Effect of storage of cement on its strength.

is greater for the first three months of storage than for latter three months periods. It was also found that the earlier tests showed a much greater loss in strength due to storage than tests at later ages.

Chemical analyses made during this investigation show that the deterioration of cement in storage is due to absorption of atmospheric moisture which in time causes a partial hydration of the cement. Fig. 199 gives a graphic summary of the results of this experiment and illustrates the falling off in strength due to storage.

These experiments were made on a small quantity of cement. The rate of seasoning of a large quantity of cement stored in bulk in a silo or bin at the plant would not be so rapid. Manifestly cement stored in a low rectangular bin would season much more slowly than if stored in sacks around which the air could circulate. Similarly the seasoning in a tall silo would be less rapid than in a low bin. The rate of seasoning would depend on the surface exposed to the atmosphere and the humidity and temperature of the latter.

Observations which the writer has made seem to indicate that the same phenomena holds good for the seasoning of clinker also and that cement made from seasoned clinker if ground to the same degree of fineness will not show the same strength as that made from the same clinker ground immediately after burning. In considering the effect of seasoning clinker on the strength of cement, it should be remembered, however, that seasoning of the clinker makes this easier to grind and consequently allows a finer product to be economically made.

Drop in Tensile Strength

A point which has often been brought against cement, and American cements in particular, is that there is a permanent drop in tensile strength after the twenty-eight day neat test. In fairly quick-setting cements with their usual low-lime content and to which the normal amount of gypsum or plaster has been added, this drop is rarely met with and is probably then due to improper

manipulation of the test. In cements high in lime, without being necessarily unsound, or in cements to which a large addition of plaster or gypsum has been made, this drop is often met with. In unsound cements it is usually met with, often after the seven-day test.

It does not necessarily follow that any drop in strength indicates a disrupting action, because as cement briquettes get older they get more and more brittle, and consequently tensile stresses break them more easily. Particularly is this true if the clips

TABLE LXIX.—Showing Loss in Strength of Neat Briquettes and Gain in Sand Briquettes After Seven-Day Test.

Cement No.	Boiling test	Tensile strength									
		Neat					1 : 3 sand				
		7 days	28 days	3 mos.	6 mos.	1 yr.	7 days	28 days	3 mos.	6 mos.	1 year
1	O. K.	657	615	650	680	711	240	302	360	381	405
2	O. K.	915	845	730	760	755	310	360	375	378	415
3	O. K.	1058	1023	890	852	783	200	263	425	410	463
4	O. K.	865	727	730	650	728	317	353	390	400	416
5	O. K.	708	656	661	663	665	201	279	402	455	520
6	O. K.	735	704	684	688	658	290	401	426	443	477
7	O. K.	916	845	816	825	802	301	360	424	450	456
8	O. K.	1012	875	890	921	944	306	374	381	410	467
9	O. K.	912	815	826	814	827	292	327	368	381	381
10	O. K.	856	803	810	814	811	275	361	369	391	418
11	Check'd	1150	775	610	615	674	235	315	366	381	427
12	"	947	816	702	310	Dis.	210	246	247	311	312
13	"	812	304	318	301	204	294	316	321	330	327
14	"	955	811	816	802	503	274	321	375	416	427
15	"	927	802	765	612	344	213	227	264	375	414
16	"	610	314	191	78	95	224	237	241	256	281
17	"	1110	765	342	Dis.	Dis.	275	298	315	362	396

exert any twisting action and the load is not evenly applied. Also cement is never used neat and in the vast majority of cases when a cement shows a slight falling off in neat strength, the sand strength increases with age. This is shown in Table LXIX. Humphreys states that the compressive strength of neat cement does not experience this drop when the cement is sound even if the tensile strength does fall off somewhat after the twenty-

eight day test; an important fact, if true, as cement is seldom if ever used in tension.

Coarse grinding of the cement has some influence on the increase in strength with age. A very fine cement increases neat very little after seven days, while a coarser one keeps on increasing. This is no doubt due to the fact that the coarse particles are acted on much slower than the fine ones, and solution and crystallization of these go on after the finer ones are all hydrated. The following experiment was made with the same cement. Cement A is just as it comes from the mills. Cement B is cement A with the coarse particles (residue on a No. 200 sieve, removed):

Age	7 days	28 days	3 mos.	6 mos.	9 mos.
Cement A, lbs.	618	695	675	725	750
Cement B, lbs.	518	546	535	510	549

Of seventy-six samples of the same brand of cement, each one containing from 63.25 to 63.75 per cent lime when freshly ground and passing the boiling test, those ground to a fineness of 80-85 per cent through a No. 200 sieve showed an increase of only 3.4 per cent neat strength between the periods of seven and twenty-eight days; while those ground to a fineness of 70-75 per cent through a No. 200 sieve gained 18.3 per cent in this time. When a cement gives a high neat break on seven days, and passes the steam test when received, failure to show a marked increase in twenty-eight days should not be taken as an indication of a poor cement.

Manufacturing Conditions Influencing Strength

The chief manufacturing conditions which influence the strength of cement are the "lime ratio," the fineness to which the cement is ground and the percentage of sulphur trioxide which it contains. The first two will play a very important part in the strength of the cement and the latter to a limited extent.

The effect of fineness on the properties of cement has been quite fully discussed. Formerly a fineness of 75 per cent passing the 200-mesh sieve was considered ample. To-day, however, a finer product is being demanded and under present conditions

most manufacturers are grinding cement to a fineness of at least 80 per cent passing the No. 200 sieve, the general range being between 80 and 85 per cent. If the cement has been properly proportioned as regards chemical composition and the setting time and soundness are satisfactory, a fineness of 80 will be ample to secure the strength required by the standard specifications. If a stronger product is desired, it will probably be found easier to secure this by fine grinding rather than by unusual chemical composition.

With regard to chemical composition, the influence of alumina in securing early strength has been discussed in Chapter II of this book. It is doubtful, however, if increasing the alumina beyond a ratio of 1 alumina to 2½ of silica will be generally advisable unless the manufacturer desires to go to the special high alumina cements. Increasing the alumina beyond this point will very probably result in quick-setting cement and difficulty in burning the clinker uniformly which would probably affect the soundness. Where the silica-alumina ratio is greater than 4 to 1, it will probably be found advisable to increase the alumina, otherwise efforts to increase strength had better be directed towards a finer cement or a higher lime ratio.

Where cement has been ground to a proper degree of fineness and does not show the desired strength, it is probable that the percentage of lime is too low. In this event, the trouble will be detected by chemical analysis and the remedy will be evident. It is, of course, difficult to give any fixed rules relative to how high the lime should be carried because this must be governed to some extent by the soundness test. Generally, however, a cement which has a lime ratio[1] of less than 1.9 will show low strength. This is particularly true of high silica cements or cements in which the alumina is low.

In connection with chemical composition it should be remembered that increasing the lime ratio will make the clinker easier to grind and consequently a finer product can be obtained with the same expenditure of power, etc.

[1] $\frac{\%\ \text{Lime}}{\%\ \text{Silica}+\%\ \text{Alumina}+\%\ \text{Iron oxide}}$ should not be less than 1.9.

Increasing the percentage of sulphur trioxide will often result in a slight gain in strength. As a general thing, if the cement has been properly proportioned the necessary strength will be obtained with a percentage of sulphur trioxide not exceeding 1.5. In extreme cases if found to be of assistance in increasing strength and where other means are not available, the percentage of sulphur trioxide in the cement might be increased with this end in view. Generally, however, it will be better to secure the strength by increasing the fineness or the lime ratio.

MISCELLANEOUS

CHAPTER XXV

THE DETECTION OF ADULTERATION IN PORTLAND CEMENT

The detection of adulteration in Portland cement is a problem which the American chemist rarely, if ever, has to solve. The writer does not recall a single instance which has come under his observation during the last fifteen years where cement has been even suspected of being adulterated. Some twenty years ago a few manufacturers at times did grind together a mixture of Rosendale or Natural cement clinker, and sell either as a blend ("Improved Cement") or sometimes as straight Portland cement. While depreciating this practice, it is only fair to the manufacturers who did this to say that for the most part they honestly believed they were making a superior product by so doing. As the result of the activities of the Portland Cement Association to discourage this practice and the fact that engineers gradually came to look upon those brands of cement with suspicion whose makers even burned Rosendale cement, these blended cements have entirely disappeared from the market.

When adulteration is suspected, the cement should be subjected to a microscopic test and if evidence of this is found a more careful investigation can be made.

Cements have been adulterated with natural cement, blast-furnace slag, ground limestone, shale, ashes, etc. Some of these substances are so similar to Portland cement that chemical analysis fails to show their presence. It is, therefore necessary to direct special tests to their detection. When present in small quantities, it is probable that even such tests will fail to show positively an adulterated cement.

Microscopic Test

The microscope furnishes us with a very good means of detecting added material in cement. Butler[1] recommends that those

[1] Portland Cement, 2nd Edition, p 304.

particles which pass a 76 sieve and are retained upon a 120 sieve be examined with a low power (say one-inch) objective. The particles of pure, well-burned cement clinker of this size will then appear dark, almost black in color, resembling coke somewhat, and will possess the characteristic spongy honey-combed appearance of cement clinker. The particles of less well-burned clinker, always present in cement, will, when examined in the same way, present the same shape and structure, but will differ in color, being light brown and semi-transparent, resembling gum arabic. Intermediate products range from black to light brown. These particles are always of a more or less rounded nature. Particles of slag of the same size viewed under the same conditions differ somewhat in color, according to the nature of the slag. Usually the particles are light colored, of angular fracture, and instead of the particles presenting a rounded appearance the edges are sharp like flint. Not to be mistaken for the slag, however, are the particles of pebbles from the tube mills used to grind the clinker. These latter may be distinguished from the slag by picking out the particles in question with a pair of pincers, crushing them in a small agate mortar and treating them with hydrochloric acid. The slag is readily attacked while the débris from the pebbles is not attacked. Particles of iron from the crushers are also present in the residue caught upon the 120 sieve. These may be identified by their black metallic appearance and their behavior with the magnet. Neither of these can, of course, be considered as adulterants. Limestone and cement-rock if present are in more or less flattened particles, and the latter is always dark gray in color. Both of these may be readily detected by effervescence with dilute acids. The foreign particles may also be picked out of the residue with a pair of tweezers, ground finely and identified by chemical analysis.

Tests of Drs. R. and W. Fresenius

Drs. R. and W. Fresenius,[1] at the request of the Association of German Cement Manufacturers, made investigations into the subject of cement adulteration looking to a method of detecting the

[1] *Ztschr. anal. Chem.*, 23, p. 175, and 24, p. 66.

same. They experimented upon twelve samples of pure Portland cement from Germany, England and France, and compared the results of tests upon these with the results obtained by similar tests upon three kinds of hydraulic lime, three kinds of weathered slag, and two of ground slag. The cements were of various ages and had been exposed to the air for various lengths of time. On the next page are tabulated their experiments for comparison.

Proposed Tests

As the result of these experiments they proposed the following tests for the detection of adulteration:

1. The specific gravity.

This must not be lower than 3.10.

2. The loss on ignition.

This should be between 0.3 and 2.59 per cent; certainly not much more.

3. The alkalinity imparted to water. One-half gram of cement should not render 50 cc. of water so alkaline as to require more than 6.25 cc. nor less than 4 cc. of decinormal acid to neutralize.

4. The volume of normal acid neutralized.

One gram of cement should neutralize from 18.8 to 21.7 cc. of normal acid.

5. The volume of potassium permanganate reduced.

One gram of cement should reduce not much more than 0.0028 gram of potassium permanganate.

6. The weight of carbon dioxide absorbed.

Three grams of cement should not absorb more than 0.0018 gram of carbon dioxide.

The tests 1, 3, 4, and 5 are for the detection of slag and 1, 2, 3 and 6 for the detection of hydraulic lime.

Drs. R. and W. Fresenius also tried these tests upon experimental mixtures containing 10 per cent of slag or hydraulic lime, and in each case were able to detect the impurity.

TABLE LXX.—ADULTERATION IN PORTLAND CEMENT.

Description		1 Specific gravity	2 Loss on ignition Per cent	3 Alkalinity imparted to water by 0.5 gr. cc. of decinormal acid	4 Volume of normal acid neutralized by 1 gram cc.	5 Weight of $KMnO_4$ reduced by 1 gram mg.	Weight of CO_2 absorbed by 3 grams mg.
Portland cement,	A....	3.155	1.58	6.25	20.71	0.79	1.4
" "	B....	3.125	2.59	4.62	21.50	2.38	1.6
" "	C....	3.155	2.11	4.50	20.28	0.93	1.8
" "	D....	3.144	1.98	5.10	21.67	1.12	1.0
" "	E....	3.144	1.25	6.12	19.60	0.98	1.6
" "	F....	3.134	2.04	4.95	20.72	1.21	1.1
" "	G....	3.144	0.71	4.30	22.20	0.89	0.0
" "	H....	3.125	1.11	4.29	20.30	1.07	0.7
" "	J....	3.134	1.00	4.00	19.40	2.01	0.0
" "	K....	3.144	0.34	4.21	20.70	0.98	0.0
" "	L....	3.154	1.49	4.60	18.80	2.80	0.3
" "	M....	3.125	1.25	5.50	20.70	2.33	0.0
Hydraulic lime	A....	2.441	18.26	20.23	21.35	1.40	27.8
" "	B....	2.551	17.82	22.73	26.80	0.93	31.3
" "	C....	2.520	19 60	19.72	19.96	0.98	47.7
Weathered slag	A....	3.012	0.76	0.91	14.19	74.60	3.6
" "	B....	3.003	1.92	0.70	13.67	60.67	3.5
" "	C....	2.967	1.11	1.00	9.70	44.34	2.9
Ground slag	I....	3.003	0.32	0.31	3.60	64.40	2.4
" "	II....	2.873	0.43	0.11	8.20	73.27	2.2

Carrying Out the Tests

The methods employed for carrying out the tests were as follows:

1. They used for taking the specific gravity the method of Schumann with turpentine as the liquid. The end of the tube was corked to prevent evaporation, the temperature kept constant, and the vessel carefully shaken to displace air bubbles. Le Chatelier's apparatus would answer as well, however, with kerosene for the liquid.

2. For the loss on ignition, 2 grams of cement were weighed into a tarred crucible, and then heated over a Bunsen burner for twenty minutes. The loss shown on again weighing was the loss on ignition.

3. For the "alkalinity to water test." The substance was finely powdered and passed through a sieve of 5,000 meshes to the square centimeter.[1] Of the resulting powder, 1 gram was shaken up with 100 cc. distilled water without warming for ten minutes. The solution was then passed through a dry filter-paper into a dry vessel and 50 cc. of the filtrated titrated with decinormal hydrochloric acid.[2]

4. "For "standard acid necessary to decompose." One gram of the fine powder obtained in 3 was shaken with 30 cc. of normal hydrochloric acid[3] and 70 cc. of water for ten minutes, with out warming, and filtered through a dry filter-paper 50 cc. of the filtrate were then titrated with normal caustic soda.[4]

5. For the volume of permanganate reduced. One gram of the fine powder, obtained in 3, was treated with a mixture of 50 cc. of dilute sulphuric acid (sp. gr. 1.12) and 100 cc. of water. The resulting solution was then titrated with potassium permanganate solution.[5]

6. For carbon dioxide absorbed, about 3 grams of the fine powder obtained as in 3, were placed in a weighed tube and a stream of carbon dioxide allowed to pass over it. The sample was then dried in a desiccator over sulphuric acid (sp. gr. 1.184) and weighed. The increase in weight gave the amount of carbon dioxide absorbed, a small calcium chloride drying tube was placed after the tube containing the cement to absorb any water evolved.

[1] 32,260 meshes to the square inch. The standard 200 mesh sieve will answer.

[2] To make decinormal hydrochloric acid, refer to page 505, with the notes under this section, and taking such a quantity of dilute hydrochloric acid as contains 3.65 grams of HCl, dilute this volume to 1 liter. Check its value by one of the methods given in the section referred to. The $^2/_5$ N nitric acid may be diluted to $^1/_{10}$ N strength and used in place of the $^1/_{10}$ N hydrochloric acid.

[3] Normal acid should contain 36.5 grams HCl per liter.

[4] To prepare normal caustic soda, refer to page 504, and using the above normal acid as a standard proceed as directed there. The $^2/_5$ N solutions used in checking the per cent of lime in cement mixture (see page 504) may be used for this test. In this case shake up the cement with a mixture of 75 cc. of $^2/_5$ normal acid and 25 cc. of water, and titrate back with the $^2/_5$ normal alkali.

[5] Dissolve 0.28 gram of $KMnO_4$ in 100 cc. of water. Not much more than 1 cc. of this solution, or 2 cc. of the solution used to determine ferric oxide in cement should be required if the cement is unadulterated.

Le Chatelier's Test

Le Chatelier has devised a very neat test for the adulteration in cement, depending upon the lower density of the adulterant than of the cement. His method consists in separating these lighter impurities from the cement by means of a heavy liquid, a mixture of methyl iodide and benzine, prepared of such strength that they float upon its surface while the pure Portland sinks to the bottom.

This method was in use in the Philadelphia City Testing Laboratory and gave good satisfaction there, where it was used to detect additions of Rosendale to Portland cement.[1]

Preparation of the Heavy Liquid

As the first step the methyl iodide solution must be prepared. This should be of density 2.95 according to Le Chatelier. As the density of the methyl iodide itself is 3.1, benzine must be added in small quantities until a crystal of aragonite (serving as a guide) whose density is 2.94 just remains at the surface. Since very small quantities of benzine change the density of the methyl iodide considerably it is well to make two solutions, one a little above and one a little below the density sought, and then to add the one to the other until the required density is obtained. By this means a more gradual change is affected and the danger of overrunning the mark is lessened.

Fig. 200.—Separatory funnel for methyl-iodide solution.

[1] Taylor, *Chem. Eng.*, I, 258.

Apparatus

Le Chatelier used in his experiments a little glass tube 10 mm. in diameter and 70 mm. long. The tube (Fig. 200) is widened at the top to a funnel and drawn at the bottom with a regular slope to an opening of 1 mm. diameter. This opening is closed on the interior a little above the bottom by a plunger consisting of a small emery ground-glass stopper on the end of a glass rod which projects above the funnel top.

Test

To make a test the stopper is wet with water or glycerine to make a tight joint and inserted into the opening of the tube. Grease cannot be used as it is dissolved by the methyl iodide solution. Ten grams of the suspected cement are weighed into the tube and 5 cc. of methyl iodide solution (sp. gr. 2.95), prepared as above, poured upon it. A thin platinum wire bent into a loop around the plunger is then moved around and up and down in the liquid in a lively manner in order to drive out all bubbles and mix the cement and liquid thoroughly. The apparatus is now set aside for an hour, when it will be found that the slag is on top and the cement below. The apparatus is now placed over a dry filter, the stopper raised and the cement and part of the liquid allowed to run out. The cement is retained upon the filter while the liquid is caught in a vessel below and may be used again. The slag and the rest of the liquid are then run out upon another filter, and the excess of liquid caught in a vessel for use again. The filters containing the slag and cement are washed with benzine, dried and weighed separately. From the weights the percentage of adulteration can be calculated. The slag and cement can then be analyzed chemically, if thought necessary, as a further guide.

CHAPTER XXVI

THE INVESTIGATION OF MATERIALS FOR THE MANUFACTURE OF PORTLAND CEMENT

Prospecting Limestone and Cement-Rock Deposits

Properties upon which it is intended to build a cement plant should be very carefully prospected, to determine not only the quality but also the quantity of the materials available. The author prefers to do this in all cases by drilling. Many geologists contend there are properties where this is mony wasted. When we consider, however, that the building of a modern cement plant entails an expenditure of seldom less than $1,000,000 and that a thorough drilling of a property can usually be done for less than $5,000, it would seem wisest always to take the precaution of doing this. The author has met with, in his personal experience, a number of instances where expert geologists had passed upon properties as containing inexhaustible quantities of material suitable for cement manufacture, which after being drilled were found conclusively to contain only very small deposits. In one instance, a mill was built and it was found on opening up the limestone beds that the deposit which they had intended to use was highly magnesian and instead of having to go only a few miles for this material, it was necessary to go twenty miles away from the plant before suitable low magnesian limestone could be found. This property was passed upon by a well known economic geologist.

The author does not think it would be possible to form any conclusion as to cement-rock without drilling. In this case, surface samples nearly always show a very much higher percentage of lime than is contained by the main body of the rock. In many places throughout the Lehigh belt, the cement-rock is overlaid by a thin skin of limestone. Five per cent of carbonate of lime will make the difference between an economical proposition and one which is not, and represents usually about ten cents per barrel in the cost of manufacture. A very accurate estimate should be made as to the quality of the rock throughout the deposit in order

that the quantity of limestone required to bring the cement-rock up to the proper composition for the manufacture of Portland cement may be determined.

The prospecting may be done by means of either a core or churn drill. In sinking the test holes, the surface dirt and clay should be shoveled away and the rock exposed. The drill can then be set up and the samples taken. The hole should be protected from surface dirt, etc., by placing a pipe from the entrance of the hole in solid rock to a few inches above the ground.

In prospecting a property, it is customary to make a map showing the topography, etc., and this should be divided into squares having sides of say 50 to 300 feet according to the uniformity of the material. Drill holes can then be sunk at the corners of each square and the cores or chips brought up by the drill saved for analysis. Usually it is the custom, instead of making one sample of all of the rock brought up from a hole, to make several samples of the material brought up from various depths. These samples should be so taken that every inch of rock through which the drill passes will be represented in the sample. Thus one sample should represent material brought up from a depth of from 0 to 5 feet, while the next should represent that taken by the drill in going from 5 to 10 feet, etc. By doing this, the uniformity of the deposit, as well as its freedom from bands of magnesian

Fig. 201.—Cross section showing limestone deposit.

stone, etc., can be tested. After the analyses are all made, charts should be drawn showing the quality of the rock at various depths, and if the drilling is carried far enough, the depth of the deposit at each point. This can be shown easiest by means of

sections, cutting the deposit along the line of squares, drawn to scale and showing by means of various kinds of shading the stripping, etc. From these charts the amount of rock available and the dirt which must be removed to get at this can be calculated. Such a chart is shown in Fig. 201.

In sampling with the churn drill the chips or mud from this should be dumped into a large tub and when all of these from a given portion of the hole have been placed in this the mud should be stirred up well and an average sample of this taken. This mud sample may be placed in a shallow tin pan and dried on the boiler of the drill, after which it should be sent to the laboratory in clean bags of cloth or paper or in tin boxes. In the laboratory, the sample should be ground and quartered down to laboratory dimensions and the final sample made to pass a No. 100 mesh sieve.

Core drillings are also much used in prospecting limestone. These cut a round cylinder or core of rock from 1 to 2 inches in diameter, as they pass into the rock. They may be obtained run by either steam, gasoline or electricity. For some purposes these cores are very valuable as they allow a minute inspection of the beds as to stratification, etc., and any thin bands of foreign material, such as quartz are shown. The machines themselves, however, are expensive and troublesome to operate as the cutting is usually done by diamonds set in the ends of the drill. Recently a number of core drills have been brought out which use a steel cutting edge. These, however, are less efficient than the diamond drill and generally speaking, in spite of lower first cost, are no more economical in the long run than the diamond drill.

In some instances less drilling would have to be done by a core drill than by a churn drill, as the churn drill can only be used to sink a vertical hole while the core drill can be used for one at any angle. For instance, by referring to Fig. 202 which is a section across a limestone deposit with a strike of about 45°, it will be seen that if we prospect with a churn drill, we would have to drill in the direction shown by the line AC, or across the beds at an angle, while if we used a core drill the drilling could be done

along the line AE, or perpendicular to the beds, which would give us a sample of exactly the same beds as along the line AC. In this case the churn drill would give us just as good a sample as the core drill but the amount of drilling required to penetrate all the beds, as will be seen, is much greater. In the case of a limestone deposit with a practically vertical pitch, the only method of drilling which can be employed to advantage is a core drill,

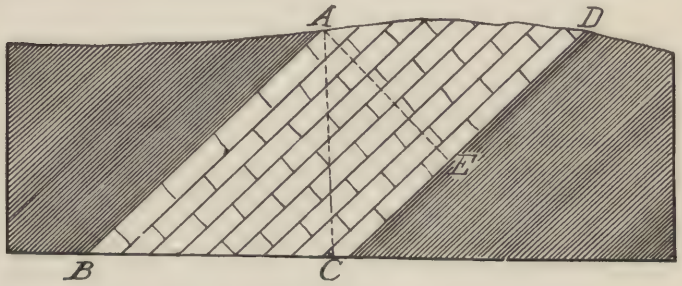


Fig. 202.—Strata pitched at an angle.

as this can be used to sink holes at right angles to the strike of the deposit, while the churn drill would penetrate only a few beds.

Some authorities contend that in sampling limestone pitched at an angle such as that shown in Fig. 202, it would be unnecessary to drill and all that is necessary would be to take surface samples along the line AD. It is highly probable that where the limestone beds are exposed either as shown in this illustration or Fig. 203 that very accurate conclusions as to both the quality and the quantity of the deposit can be formed by sampling along the lines AD. Where conclusions have to be drawn, however, upon data of this sort, the services of an expert should always be employed, as considerable experience is necessary in order that false and misleading conclusions may not be drawn.

In calculating the quantity of material available it is sufficiently accurate for ordinary purposes to assume that one ton of material as quarried will produce 3.3 barrels of cement. If the mixture is four-fifths limestone and one-fifth shale, then four-fifths ton of limestone will produce 3.3 barrels, or one ton of

limestone will produce 4.1 barrels of cement and one ton of shale will produce 16.5 barrels of cement. For practical purposes it may also be assumed that one cubic foot of limestone will weigh 160 pounds and that a cubic foot of shale will weigh 125 pounds. The actual weights may be determined by taking the specific gravity of the stone and multiplying this by 62.4, which will give the weight in pounds of a cubic foot of solid material.

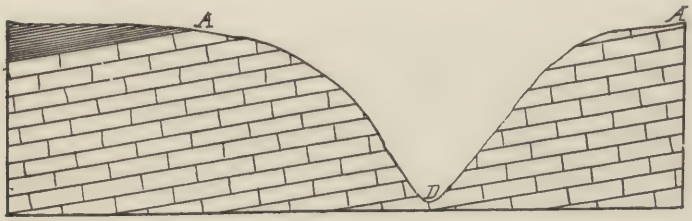


Fig. 203.—Strata exposed by ravine.

Roughly speaking, each acre of limestone will produce 14,290 barrels of cement for each foot in depth and one acre of shale will produce 57,500 barrels of cement for each foot in depth, when the proportions between the two are 5 to 1. That is, a property ten acres in area with a limestone deposit 100 feet deep will produce 14,290,000 barrels of cement when the limestone is mixed with one-fifth its weight of shale. Referring again to Fig. 202, which illustrates the cross-section of a limestone deposit pitched at an angle, it may be noted that in calculating the quantity of limestone available, it is not correct to consider the parallelogram ABCD as a cross-section of this. The cross-section of the available stone is represented by the triangle ACD, since manifestly it would not be possible by open quarrying methods to get out the rock lying in the wedge ABC, when overlaid by such loose material as shale, for example.

Clay and Shale

Clay can be sampled in a number of ways, such as by digging pits or sinking test holes by means of a soil sampler, auger drill or a serrated pipe. Hard clays and shales will require either

the auger, diamond or churn drill. The auger drill, for use in sampling, is similar to those used for coal cutting, etc. The serrated pipe consists of a pipe, the end of which has been filed and tempered to form sharp teeth like a saw. This is forced down into the clay by twisting a handle at the upper end. The result, when withdrawn, is a plug of clay, filling the pipe and representing the strata through which the latter has passed. The soil sampler consists of a short auger 6 inches long and about 4 inches in diameter mounted on a long jointed iron rod provided with a wooden handle at its upper end. It may be purchased of houses dealing in laboratory supplies. It is used similar to the pipe and a plug of clay is obtained on the auger. The rod is usually jointed in lengths of a yard.

An ordinary post hole digger may also be used for sampling clay.

Clay deposits should be mapped out carefully, as different parts of the bed may show very different proportions of silica and alumina, and in order to get a cement with uniform setting properties it may be necessary to work two or more parts of the deposit in conjunction, to keep the ratio between the silica and alumina constant.

The depth of the deposit should also be determined so that a calculation of the available quantity of clay may be made.

Marl

For sampling marl, a tube, similar to that used for sampling cement, may be employed to advantage. This is described on page 548, or the serrated pipe described before may be used. If the marl deposit is very wet, a long pipe having a plug at one end may be used. This plug should be of iron, have a sharp point, fit the mouth of the pipe closely and be fastened to a long thin iron rod. In using the sampler, the iron plug is drawn up against the mouth of the pipe and the latter is thus shoved down to the depth at which the sample is to be taken. The pipe is then raised and shoved down to its former level, being forced tight against the iron plug. The pipe is then raised by means of the rod and the sample dumped out.

If the marl is fairly dry the soil sampler described above may be used.

Marl deposits should be very thoroughly mapped out, not only as to quality but also as to the depth of the deposit in order that the quantity available for manufacturing purposes may be calculater, since the value of marl deposits depends in most cases as much upon quantity as quality.

Trial Burnings

In prospecting new deposits of raw materials, it is sometimes thought advisable to make up small trial lots of cement in the laboratory and examine into the physical properties of these. For such trials, it is necessary to crush the raw materials, if they are not already in small pieces, and correctly proportion them. The mixture is then finely ground, the powder moistened with water and moulded into little cubes or balls and these latter are burned in some form of laboratory kiln. The resulting clinker is then sorted to separate out the under-burned, and the hard-burned portions are ground to the same degree of fineness as commercial cement. It is also often desirable to make experimental burnings in the investigation of the various problems which arise in connection with the manufacture and properties of cement. The apparatus described below is suitable for such purposes and has been used in similar work by various investigators.

For crushing the raw rock small Blake or Bosworth crushers such as are used in almost all laboratories for crushing ores will be found convenient. These can be so adjusted as to crush the rock to about wheat size and finer. They can be obtained either hand or power driven, but for the work indicated above they should be power driven and attached to a shafting somewhere about the mill or run by an independent motor. After crushing the materials to the size indicated above they should be carefully analyzed and mixed in the proper proportions (see Chapter IV). The mixture should then be finely ground. The degree of fineness should be indicated by the nature of the investigation. If a test is being made of the suitability of certain raw materials the

mixture should be ground no finer than it would be in actual mill practice, or about 95 per cent through a 100-mesh sieve.

Samples of clay and marl should be thoroughly dried before analyzing and proportioning them. This can be done over a hot plate or steam radiator, etc.

For finely grinding the mixture, a jar mill will be found as convenient as anything else. Fig. 204 shows the form (made by the Abbé Engineering Company) which the writer has used in his laboratory and found very satisfactory. This consists of a porce-

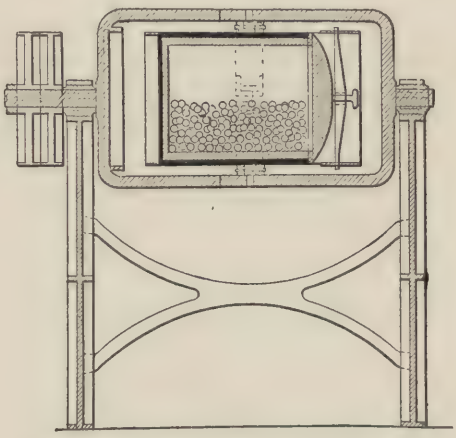


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Fig. 204.—Jar mill.

lain jar, the cover of which is fastened tightly on by means of a clamp, as shown. The jar itself is held in a revolving frame by brass bands, one of which can be loosened by means of a thumb screw, allowing the jar to be removed from the frame. The jar is filled half full of porcelain balls and as the former revolves the material is ground by the latter. The jar is intended to make from forty to fifty revolutions per minute and will grind about 15 pounds of material at a charge.

After grinding finely, the powder is mixed with water until it is plastic and then molded into small cubes or balls. The writer has usually found it an excellent plan to roll the mass out in a

thin sheet on a pane of glass or an oiled board and then cut this into blocks with the point of a spatula or trowel. The size of the balls or cubes will depend upon the size of the furnace—a small furnace will require a smaller ball than a larger one. They should not, however, be smaller than a pea for even a small furnace.

Experimental Shaft Kilns

For burning small quantities of cement the writer has found

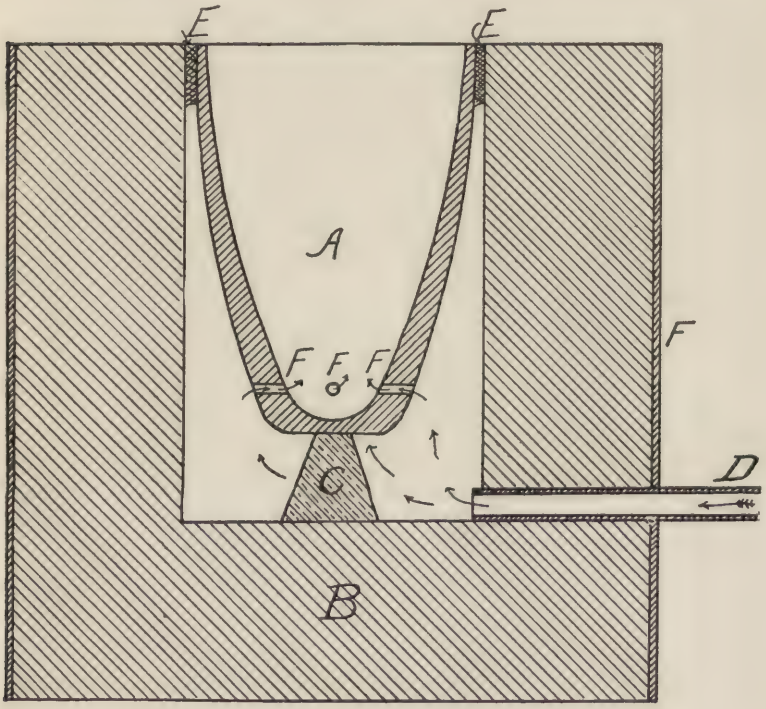

Fig. 205.—Furnace for experimental burnings.

the form of kiln shown in Fig. 205 useful. It consists of a large Battersea crucible (size R) 13 inches in height and 10 inches in

diameter, resting on a piece of fire-brick, C, and fitting snugly into a cylinder of concrete, B. The crucible is punched with four holes F, F, F, F, around its bottom and through these the air for combustion enters the crucible. A tight joint between the crucible and the concrete cylinder is made by means of fire-clay or wet asbestos as shown at E, E. Air is brought into the concrete cylinder by means of the pipe D. F, F, is a sheet iron jacket surrounding the cylinder of concrete. The walls of the cylinder are about 6 inches thick. Air for burning may be obtained from a compressor or a small Root or Crowell blower. Larger crucibles than the size indicated can be obtained when a larger furnace is needed. The one given above will burn 3 or 4 pounds of cement. Charcoal or oil coke is used as a fuel. A small piece of cotton waste saturated with oil is placed in the crucible and when this is burning a few handfuls of charcoal are added and the air blast turned on. As soon as the charcoal is burned and the crucible is heated up, it is filled half full of charcoal and the little balls of slurry are added in a thin layer. More charcoal is placed over this and then more slurry, etc., until the crucible is full. A pair of fire-bricks having an inch channel cut in one side of each is then placed over the crucible to form a cover and the heating continued until all the charcoal is burned away. The air is left turned on to cool the clinker after which the latter is sorted.

Another form of furnace which the writer has used in his laboratory of recent years is shown in Fig. 206. This consists of a small cylinder of boiler iron *a* (which by the way was part of an old stack) lined with fire-brick. This is provided with an iron plate, *b*, perforated with holes as shown. The opening *c* below the grate is closed by means of a cast-iron door and the cracks around this are plastered tight with clay, or better still wet asbestos paper, which can be rammed into the cracks very tightly. Air is blown in at *d* by means of a fan or pressure blower. In using the furnace, a little broken fire-brick, in pieces about an inch in size, is placed on the wrought iron plate to prevent this being damaged by the heat. Fire is kindled upon this, charcoal being used as fuel, the burning being conducted

just as described above. When the burning is completed, the iron plate is tilted so as to allow the clinker and ashes to drop into the pit beneath. From this it is drawn out through the opening *c* by means of a small scraper, sorted and ground.

For research work when contamination with the fuel ash is objectionable, a small Fletcher furnace lined with a mixture of

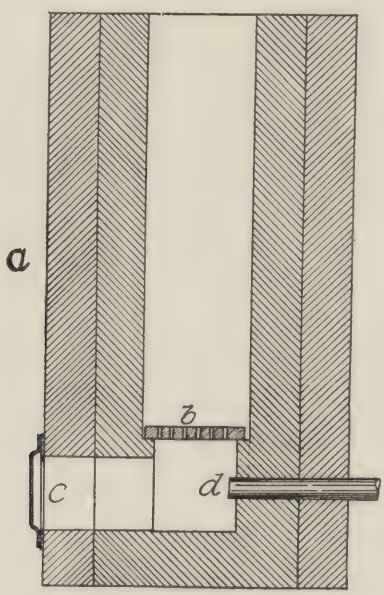

Fig. 206.—Shaft kiln for trial burnings.

ninety parts coarse, burned magnesite and ten parts Portland cement will be found useful.

Bleininger describes[1] a kiln used in the Ohio State University Ceramic Department. This consists of a straight shaft of firebrick with walls 4 inches thick, divided into three distinct divisions. Air is forced into a space 4 inches high at the bottom under a pressure of about 12 ounces from a blower through a 2-inch pipe. This space is divided from the next division by means of a cast-iron plate provided with concentric rows of holes.

[1] *Ohio Geol. Survey Bul. No. 3* (IV) Manufacture of Hydraulic Cements.

Above this plate about 5 inches away from it an iron pan is supported by two bricks. Petroleum is fed into this pan by means of a ¼-inch pipe, running in by gravity from a can some distance away. Several inches above the pan the whole cross-section of the shaft is filled with broken fire-brick. Above this compartment the third compartment is formed by a grating of bricks, made of a mixture of 80 per cent magnesite and 20 per cent Portland cement. On this grating the balls of cement mixture are heaped up to the top of the compartment, which is about 8 inches high. The cover consists of a perforated clay tile upon which are piled broken bricks. The clinker compartment is accessible from the outside by means of a door which is closed by a fire-brick plug which can be removed and the clinkers withdrawn and examined.

To start the furnace, a small amount of paper and wood is placed upon the pan through a hole provided for this purpose. The oil on coming in contact with the hot pan is vaporized and mixes with the air in the compartment filled with broken brick. The time required for a burn in this kiln is about two hours. By removing the pan, bricks and broken pieces of brick this kiln can also be used for burning with coke.

When large quantities of cement are to be burned a small shaft kiln made of fire-brick and provided with grate bars can be used. The cement mixture and coke being charged in alternate layers after the furnace is well heated up and a bed of hot coals is obtained on the grate bars. The temperature of such a kiln can be greatly increased by providing means of blowing air through the grate bars.

Experimental Rotary Kilns

Prof. E. D. Campbell, of the University of Michigan, used in his experimental work a small rotary kiln consisting of an iron pipe, 8 inches in diameter and 32 inches long. This was lined with four sections of hard-burned magnesite pipe, 3 inches internal diameter, and was revolved by means of a ½-horsepower motor, at a speed of one revolution in eighty-five seconds. It was fired by means of a Hoskins gasoline burner under an air pressure of 50 pounds.

The writer at one time had an experimental laboratory which was equipped with the following apparatus.

1—2″ x 6″ Roll Jaw Crusher (Sturtevant Mill Co., Harrison Square, Boston Mass.). Used for preliminary crushing to ½″ and under.

1—4″ x 6″ Laboratory Rolls (Sturtevant Mill Co.). Used for crushing to ⅛″ and under.

1—30″ x 36″ Pebble Mill (Abbé Engineering Co., New York). Capacity 300 lbs. per charge, used for pulverizing the raw materials.

1—2′ x 20′ Rotary Kiln (Vulcan Iron Works). Fire Brick Lining (Harbison-Walker, Pittsburgh, Pa.). Used for burning. Kiln was heated by an oil burning system (Rockwell Furnace Co., N. Y.).

1—24″ x 24″ Pebble Mill (Abbé Engineering Co.). Capacity 180 lbs. per charge. Used for grinding clinker.

1—Backus, 12 H. P. Gasoline Engine for Power.

This experimental plant was sufficiently large to allow manufacturing 500 or 600 pounds of cement per day of eight hours.

An excellent experimental kiln can be made from a piece of 12- to 16-inch wrought iron pipe. This should be about 10 feet long. Nothing is gained by making the kiln longer than this. The idea of a long kiln is, of course, to save fuel and any figures on fuel required by such a small kiln are no indication of what will be required in practice. The kiln can be lined by having round fire tile 2 inches thick made to fit in the tube. An easier way, however, is to make a wooden core about 6 inches smaller than the diameter of the pipe and ramming in between the pipe and this core a mixture of any of the fire resisting cements such as "Sil-O-Cel, C_3," and Portland cement. Two wrought iron bands, 1 inch by 1 inch, should be shrunk on the pipe to answer for riding rings or tires and these should be turned in a lathe on both sides and wearing surface to make them true.

It is not necessary to employ a girth gear in order to revolve the kiln as this may be done by revolving the rollers on which the tube rests. The roller should be about 4 inches in diameter and the upper set should be provided with flanges one-half inch

deep, between which the riding ring rests in order to keep the tube from riding off. The power is usually applied to two rollers by using a common shaft for the two rollers on one side. Or the two upper rollers may be hitched together by means of a loop of chain belting.

These small kilns revolve at a considerably higher rate of speed than the large kilns and generally it is not necessary to revolve them slower than four or five turns per minute. If operated from a motor it will be necessary, of course, to reduce the speed considerably and this can be done easiest by means of a small worm gear and one or two jack-shafts.

The whole apparatus should be mounted on a table, setting the kiln on top and the motor, worm gear and any jack-shafts on a shelf underneath. The desired inclination can be secured by blocking up the table at the feed end of the kiln. The table top should be protected from the heat by heavy asbestos board.

For heating the kiln, an oil burner will be found most satisfactory. If compressed air is obtainable the oil may be stored in a closed tank and forced to the burner by pressure. Compressed air will also prove serviceable for atomizing. Where compressed air is not available the oil can be placed in a tank or barrel 10 or 15 feet above the kiln and the air for atomizing can be obtained by using a Root or Crowell positive pressure blower. Fuel oil may be used but as the matter of expense is not very great, kerosene will probably be found more convenient. Fuel oil often has to be heated in order to make it atomize readily and it also contains sediment which may stop up the burners.

The writer has usually fed the kiln by hand, placing the material to be burned in the upper end by means of a spoon or shovel with a long handle. In order to do this it has generally been found more convenient to place the upper end of the kiln under a hood and stack rather than to attempt to close it in, as with larger kilns. No doubt automatic means for feeding could be very simply devised, but a small kiln of this sort requires constant attention, in any event, and hence it will probably be found just as satisfactory in the long run to feed by hand every five or ten minutes.

The material to be burned can be easiest handled if it is moistened thoroughly with enough water to make it cohere, otherwise it is apt to blow out of the kiln.

After sorting the clinker it is crushed and ground in the jar mill mentioned before, the degree of fineness being regulated by conditions. Plaster or gypsum must, of course, be added to slow the set of the resulting cement and may be ground in with the clinker.

Value of Experimental Burnings

The writer is disposed to doubt the value of experimental burnings in determining the value of any given raw material. The suitability of materials for the manufacture of cement usually depends upon their chemical composition, accessibility, ease with which they can be ground, regularity of the deposit, etc.

In the manufacture of cement on a small scale the chemical composition, fineness and uniformity of the mixture fed to the kilns and the temperature and duration of the seasoning itself are under such perfect control that many materials can be satisfactorily manufactured into cement under such conditions which would be unsatisfactorily for use in actual practice. The writer believes that in research work test burnings are of undoubted value, but for determining the value of a cement property they are of no actual help unless there is some peculiarity in the chemical composition of the raw materials. For instance, the writer once made an investigation of raw materials containing 2 per cent of salt (NaCl) to determine if this latter would practically all volatilize in the kiln, and found it would. As has been said, the important points are: (1) Is the material of the proper chemical composition to make good cement. The limits for this have been well established. (2) Can it be gotten out economically and sent to the mill of substantially uniform composition (particularly so far as the silica-alumina ratio goes) from day to day? (3) Can it be ground to the required degree of fineness. (4) Is the deposit of suitable material extensive enough to warrant exploiting? For determining these points the judgment of a cement expert (with a practical, not literary knowledge of the subject) should be sought.

APPENDIX

Tables

TABLE LXXI.—THE ATOMIC WEIGHTS OF THE MORE IMPORTANT ELEMENTS. O = 16.

Name	Symbol	Weight	Name	Symbol	Weight
Aluminum	Al	27.1	Iron	Fe	55.85
Antimony	Sb	120.2	Lead	Pb	207.10
Arsenic	As	74.96	Magnesium	Mg	24.32
Barium	Ba	137.37	Manganese	Mn	54.93
Bismuth	Bi	208.0	Mercury	Hg	200.00
Boron	B	11.0	Nickel	Ni	58.68
Bromine	Br	79.92	Nitrogen	N	14.01
Cadmium	Cd	112.40	Oxygen	O	16.00
Calcium	Ca	40.09	Phosphorus	P	31.00
Carbon	C	12.00	Platinum	Pt	195.00
Chlorine	Cl	35.46	Potassium	K	39.10
Chromium	Ch	52.0	Silicon	Si	28.03
Cobalt	Co	58.97	Silver	Ag	107.88
Copper	Cu	63.57	Sodium	Na	23.00
Fluorine	F	19.0	Strontium	Sr	87.62
Gold	Au	197.2	Sulphur	S	32.07
Hydrogen	H	1.008	Tin	Sn	119.00
Iodine	I	126.92	Zinc	Zn	65.37

TABLE LXXII.—FACTORS.

Found	Sought	Factor	Found	Sought	Factor
Lime			*Sulphur*		
CaO	$CaCO_3$	1.78443	$BaSO_4$	S	0.13738
$CaCO_3$	CaO	0.56040	$BaSO_4$	SO_3	0.34300
$CaSO_4$	CaO	0.41195	$BaSO_4$	$CaSO_4$	0.58327
$CaSO_4$	$CaCO_3$	0.73508	$BaSO_4$	$(CaSO_4)_2H_2O$	0.62184
CaS	CaO	0.77916	$BaSO_4$	$CaSO_4 2H_2O$	0.73756
CaS	$CaSO_4$	1.88720	$BaSO_4$	CaS	0.30909
CO_2	$CaCO_3$	2.27472	$BaSO_4$	H_2SO_4	0.42016
MgO	CaO	1.39000	CdS	S	0.52193
			CdS	CaS	0.49825
Magnesia			*Alkalies*		
$Mg_2P_2O_7$	MgO	0.36219	K_2PtCl_6	K_2O	0.19384
$Mg_2P_2O_7$	$MgCO_3$	0.75744	K_2PtCl_6	KCl	0.30686
MgO	$MgCO_3$	2.09129	$NaCl$	Na_2O	0.53028
CaO	MgO	0.71943			
$MgCO_3$	MgO	0.47818	*Miscellaneous*		
CO_2	$MgCO_3$	1.91636	$AgCl$	HCl	0.25442
			CO_2	C	0.27273
			$Mg_2P_2O_7$	P_2O_5	0.63780
Iron					
Fe	Fe_2O_3	1.42971			
Fe	FeO	1.28650			
Fe_2O_3	Fe	0.69943			
Fe_2O_3	FeO	0.89983			

TABLE LXXIII.—For Converting $Mg_2P_2O_7$ to MgO.

Percentage of MgO 0.5 gram sample	Grams of $Mg_2P_2O_7$ weighted									
	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
1.00	.0138	.0139	.0141	.0142	.0144	.0145	.0146	.0148	.0149	.0151
1.10	.0152	.0153	.0155	.0156	.0158	.0159	.0160	.0162	.0162	.0164
1.20	.0166	.0167	.0168	.0170	.0171	.0173	.0174	.0175	.0177	.0178
1.30	.0180	.0181	.0182	.0184	.0185	.0186	.0188	.0189	.0191	.0192
1.40	.0193	.0195	.0196	.0197	.0199	.0200	.0202	.0203	.0204	.0206
1.50	.0207	.0209	.0210	.0211	.0213	.0214	.0215	.0217	.0218	.0220
1.60	.0221	.0222	.0224	.0225	.0226	.0228	.0229	.0231	.0232	.0233
1.70	.0235	.0236	.0238	.0239	.0240	.0242	.0243	.0244	.0246	.0247
1.80	.0249	.0250	.0251	.0253	.0254	.0255	.0257	.0258	.0260	.0261
1.90	.0262	.0264	.0265	.0267	.0268	.0269	.0271	.0272	.0273	.0275
2.00	.0276	.0278	.0279	.0280	.0282	.0283	.0285	.0286	.0287	.0289
2.10	.0290	.0291	.0293	.0294	.0296	.0297	.0298	.0300	.0301	.0302
2.20	.0304	.0305	.0307	.0308	.0309	.0311	.0312	.0314	.0315	.0316
2.30	.0318	.0319	.0320	.0322	.0323	.0325	.0326	.0328	.0329	.0330
2.40	.0331	.0333	.0334	.0336	.0337	.0338	.0340	.0341	.0343	.0344
2.50	.0345	.0347	.0348	.0349	.0351	.0352	.0354	.0355	.0356	.0358
2.60	.0359	.0360	.0362	.0363	.0365	.0366	.0367	.0369	.0370	.0372
2.70	.0373	.0374	.0376	.0377	.0378	.0380	.0381	.0383	.0384	.0385
2.80	.0387	.0388	.0389	.0391	.0392	.0394	.0395	.0396	.0398	.0399
2.90	.0400	.0402	.0403	.0405	.0406	.0407	.0409	.0410	.0412	.0413
3.00	.0414	.0416	.0417	.0419	.0420	.0421	.0423	.0424	.0425	.0427
3.10	.0428	.0429	.0431	.0432	.0434	.0435	.0436	.0438	.0439	.0441
3.20	.0442	.0443	.0445	.0446	.0447	.0449	.0450	.0452	.0453	.0454
3.30	.0456	.0457	.0458	.0460	.0461	.0463	.0464	.0465	.0467	.0468
3.40	.0470	.0471	.0472	.0474	.0475	.0477	.0478	.0479	.0481	.0482
3.50	.0483	.0485	.0486	.0488	.0489	.0490	.0492	.0493	.0495	.0497

TABLE LXXIV.—For Calculating the Percentage of Lime or Carbonate of Lime with One-Half Gram Sample.[1]

55.0 cc.		55.1 cc.		55.2 cc.	
CaO	$CaCO_3$	CaO	$CaCO_3$	CaO	$CaCO_3$
1 1.018	1.816	1 1.016	1.814	1 1.015	1.812
2 2.036	3.632	2 2.032	3.628	2 2.030	3.624
3 3.054	5.448	3 3.048	5.442	3 3.045	5.436
4 4.072	7.264	4 4.064	7.256	4 4.060	7.248
5 5.090	9.080	5 5.080	9.070	5 5.075	9.060
6 6.108	10.896	6 6.096	10.884	6 6.090	10.872
7 7.126	12.712	7 7.112	12.698	7 7.105	12.684
8 8.144	14.528	8 8.128	14.512	8 8.120	14.496
9 9.162	16.344	9 9.144	16.326	9 9.135	16.308

[1] *Chemical Engineer*, I, 42.

55.3 cc	
CaO	$CaCO_3$
1 1.013	1.808
2 2.026	3.616
3 3.039	5.424
4 4.052	7.232
5 5.065	9.040
6 6.078	10.848
7 7.091	12.656
8 8.104	14.464
9 9.117	16.262

55.4 cc.	
CaO	$CaCO_3$
1 1.011	1.805
2 2.022	3.610
3 3.033	5.415
4 4.044	7.220
5 5.055	9.025
6 6.066	10.830
7 7.077	12.635
8 8.088	14.440
9 9.099	16.245

55.5 cc.	
CaO	$CaCO_3$
1 1.009	1.801
2 2.018	3.602
3 3.027	5.403
4 4.036	7.204
5 5.045	9.005
6 6.054	10.806
7 7.063	12.607
8 8.072	14.408
9 9.081	16.209

55.6 cc.	
CaO	$CaCO_3$
1 1.007	1.797
2 2.014	3.594
3 3.021	5.391
4 4.028	7.188
5 5.035	8.985
6 6.042	10.782
7 7.049	12.579
8 8.056	14.376
9 9.063	16.173

55.7 cc.	
CaO	$CaCO_3$
1 1.005	1.794
2 2.010	3.588
3 3.015	5.382
4 4.020	7.176
5 5.025	8.970
6 6.030	10.764
7 7.035	12.558
8 8.040	14.352
9 9.045	16.146

55.8 cc.	
CaO	$CaCO_3$
1 1.004	1.792
2 2.008	3.584
3 3.012	5.376
4 4.010	7.168
5 5.020	8.960
6 6.024	10.752
7 7.028	12.544
8 8.032	14.336
9 9.036	16.128

55.9 cc.	
CaO	$CaCO_3$
1 1.002	1.789
2 2.004	3.578
3 3.006	5.367
4 4.008	7.156
5 5.010	8.945
6 6.012	10.734
7 7.014	12.523
8 8.016	14.312
9 9.018	16.101

56.0 cc	
CaO	$CaCO_3$
1 1.000	1.785
2 2.800	3.570
3 3.000	5.355
4 4.000	7.140
5 5.000	8.925
6 6.000	10.710
7 7.000	12.495
8 8.000	14.280
9 9.000	16.065

56 1 cc.	
CaO	CaCO
1 0.998	1.782
2 1.996	3.564
3 2.995	5.346
4 3.993	7.128
5 4.991	8.910
6 5.989	10.692
7 6.987	12.474
8 7.986	14.256
9 8.984	16.038

56.2 cc.	
CaO	$CaCO_3$
1 0.996	1.779
2 1.992	3.558
3 2.988	5.337
4 3.984	7.116
5 4.980	8.895
6 5.976	10.674
7 6.972	13.453
8 7.968	14.232
9 8.964	16.011

56.3 cc.	
CaO	$CaCO_3$
1 0.995	1.776
2 1.990	3.552
3 2.985	5.328
4 3.980	7.104
5 4.975	8.880
6 5.970	10.656
7 6.965	12.432
8 7.960	14.408
9 8.955	15.984

56.4 cc.	
CaO	$CaCO_3$
1 0.993	1.773
2 1.986	3.546
3 2.979	5.319
4 3.972	7.092
5 4.965	8.865
6 5.958	10.638
7 6.951	12.411
8 7.944	14.184
9 8.937	15.957

56.5 cc.		56.6 cc.		56.7 cc.	
CaO	$CaCO_3$	CaO	$CaCO_3$	CaO	$CaCO_3$
1 0.991	1.770	1 0.989	1.767	1 0.988	1.764
2 1.982	3.540	2 1.978	3.534	2 1.976	3.528
3 2.973	5.310	3 2.967	5.301	3 2.964	5.292
4 3.964	7.080	4 3.956	7.068	4 3.952	7.056
5 4.955	8.850	5 4.945	8.835	5 4.940	8.820
6 5.946	10.620	6 5.934	10.602	6 5.928	10.584
7 6.937	12.390	7 6.923	12.369	7 6.916	12.348
8 7.928	14.160	8 7.912	14.136	8 7.904	14.112
9 8.919	15.930	9 8.901	15.903	9 8.892	15.876

56.8 cc.		56.9 cc.		57.0 cc.	
CaO	$CaCO_3$	CaO	$CaCO_3$	CaO	$CaCO_3$
1 0.986	1.761	1 0.984	1.757	1 0.983	1.754
2 1.972	3.522	2 1.968	3.514	2 1.966	3.508
3 2.958	5.283	3 2.952	5.271	3 2.949	5.262
4 3.944	7.044	4 3.936	7.028	4 3.932	7.016
5 4.930	8.805	5 4.920	8.785	5 4.915	8.770
6 5.916	10.566	6 5.904	10.542	6 5.898	10.524
7 6.902	12.327	7 6.888	12.299	7 6.881	12.278
8 7.888	14.088	8 7.872	14.056	8 7.864	14.032
9 8.874	15.849	9 8.856	15.813	9 8.847	15.786

The first column of each table gives the number of cubic centimeters of permanganate required by 0.5 gram of calcite (see page 454), and the second and third columns show the corresponding percentages of calcium oxide and calcium carbonate respectively where a half gram sample has been taken.

Example of the use of tables.—Suppose 0.5 gram of calcite takes 55.6 cc. of permanganate, then write the values found in the table headed 55.6 cc. on a card and stand near the burette table. The writer usually notes the CaO values in red ink and the $CaCO_3$ in black to avoid confusing them.

Now suppose we analyze a limestone and find it requires 51.3 cc. then the percentage of lime and carbonate of lime may be calculated from the table as follows:

			CaO	$CaCO_3$
50.0	cc.	=	50.35	89.85
1.0	cc.	=	1.007	1.797
.3	cc.	=	.3021	.5391
51.3			51.6591	92.1861

TABLE LXXV.—Percentage of Water for Sand Mixture.

(Calculated from the Formula on page 649).

Neat	1-1	1-2	1-3	1-4	1-5
18	12.5	10.5	9.5	8.9	8.5
19	12.9	10.7	9.7	9.0	8.6
20	13.2	10.9	9.8	9.2	8.7
21	13.5	11.2	10.0	9.3	8.8
22	13.9	11.4	10.2	9.4	8.9
23	14.2	11.6	10.3	9.6	9.0
24	14.5	11.9	10.5	9.7	9.2
25	14.9	12.1	10.7	9.8	9.3
26	15.2	12.3	10.8	10.0	9.4
27	15.5	12.5	11.0	10.1	9.5
28	15.9	12.7	11.2	10.2	9.6

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